Final Report

On-Road Motor Vehicle Emissions including NH₃, SO₂ and NO₂

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Acknowledgements

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Abstract

The three California cities of San Jose, Fresno and west Los Angeles (LA) were visited during March 2008 to remotely collect on-road emission measurements of carbon monoxide (CO), carbon dioxide, hydrocarbons (HC), nitric oxide (NO), sulfur dioxide, ammonia (NH_3) and nitrogen dioxide (NO_2) from light-duty vehicles. A database for each site was compiled and contains 24,978 records in San Jose, 13,365 records in Fresno and 17,953 records in LA for which the State of California provided registration information. At the San Jose and LA sites repeat measurements of CO, HC and NO show large fuel specific emissions reductions between 1999 and 2008. In Fresno a small fleet of 2007 diesel ambulances was found to have more than 60% of the emitted oxides of nitrogen as NO_2. NH_3 emissions are again shown to have a strong dependence on model year with NH_3 means of 0.49 ± 0.02, 0.49 ± 0.01 and 0.79 ± 0.02 gm/kg of fuel for San Jose, Fresno and LA respectively with the larger in emissions at the LA site likely a result of the more aggressive driving mode.

Executive Summary

Mobile sources are one of the larger contributing factors that effect air quality issues in the State of California. As such, having direct knowledge of fleet averaged on-road emission levels is a critical input parameter for estimating inventories, evaluating emission control programs and planning future air improvement strategies. Toward that end the University of Denver has completed an on-road remote sensing study of motor vehicle emissions at sites in San Jose, Fresno and Los Angeles California. This is the first time that US light-duty fleets have been measured with our new multi-spectrometer instrument. A database for each site was compiled and contains 24,978 records in San Jose, 13,365 records in Fresno and 17,953 records in West Los Angeles for which the State of California provided registration information. All of the databases will be available for download from our website www.feat.biochem.du.edu.

Previous measurements existed at the San Jose site (1999) and the West Los Angeles site (1999, 2001, 2003 and 2005). The mean CO, HC and NO emissions for the fleet measured in San Jose experienced large reduction for all three species. At the West Los Angeles site previous reductions in CO and HC continued with this study, however, NO emissions increased from the 2005 measurements. Whether the increase in NO emissions is related to the change of season (fall to spring) that the measurements were collected is unclear and cannot be ruled out. Calculating emission reductions at the two sites between 1999 and 2008, finds that at the San Jose site CO, HC and NO emissions have decreased by 66%, 74% and 40% respectively despite an increase of 1.2 model years in the average age of the fleet. The West LA site has seen similar decreases of 70%, 74% and 43% for CO, HC and NO respectively while the fleet has only increased in age 0.2 model years over that period. The Fresno site had the oldest fleet at approximately 8.5 years old and is the only site where new car sales have never recovered after the 2001 downturn.

Ammonia emissions are influenced by driving mode and we observed differences between the three sites that were sampled. San Jose and Fresno had very similar fuel-based ammonia emissions with means of 0.48 ± 0.01 g/kg and 0.49 ± 0.01 g/kg while the data collected at the West Los Angeles site was higher with a mean of 0.79 ± 0.02 g/kg. The West Los Angeles site had significantly higher emissions for the newest model year vehicles and we believe that is a result of the more aggressive driving mode observed. We also observed that at all of the sites the emissions retreat with age at a similar rate. As catalyst age they begin to loose their reducing capabilities and driving mode becomes less important. This data shows that process to begin when vehicles are approximately fifteen years old. As NO_x emissions have decreased over the last twenty model years, the amount of the total fixed nitrogen emissions have also decreased. However, the fraction of these fixed nitrogen emissions contributed by ammonia have increased becoming a major component of the low fixed nitrogen emissions of the newest model years at all sites.

Light-duty measurements of NO_2 were generally expected to be rather uninteresting as gasoline powered vehicles emit little if any NO_2 and the fraction of the light-duty fleet in California that are diesels is small. However, beginning with the 2007 model year vehicles, diesel engine manufacturers were required to begin phasing in major reductions in particulate and NO_x

emissions with the full phase-in to be complete in 2010. These new regulations affect all diesel powered vehicles not just heavy-duty diesel vehicles. At the Fresno location a local ambulance company, which happened to use our ramp for their return trip from the downtown health center, provided us with measurements from new diesel particulate filter equipped vans. In total 30 2007 Dodge Sprinter vans (29 operating as ambulances) were measured 57 times over the seven days of measurements. These vans had gNO_2/kg emissions that were an order of magnitude larger than the other 865 2007 vehicles. These vehicles also had more than twice of their NO_x emissions emitted as NO_2 and while only counting for 0.4% of all the measurements they accounted for almost 15% of the sites total NO_2 emissions. While the number of light-duty diesel vehicles in Fresno is small the increased NO_2 emissions seen from these vehicles on-road might point to a future of increased on-road NO_2 emissions. This would have large ramifications for local ozone formation.

Sulfur dioxide emissions were also recorded with our new instrument and, despite changes to the analysis software; they still indicate a model year dependence that we do not fully understand. Sulfur dioxide emissions should be limited to the amount of sulfur in the fuel plus a small additional amount in older vehicles due to oil consumption. This should be reflected with most model years being at or below the fuel sulfur levels (15ppmw which translates into approximately 0.03 gSO_2/kg). We find only the newest eight to nine model years that meet these levels with older models (1999 models and older) rising to higher levels that are inconsistent with the known amounts of sulfur available for oxidation. The most logical explanation for these higher sulfur levels is some type of interference found in older vehicle exhaust that positively interferes with our SO_2 measurements. At this time we have been unable to identify this interference.

INTRODUCTION

Many cities in the United States are in violation of the air quality standards established by the Environmental Protection Agency (EPA). Carbon monoxide (CO) levels become elevated primarily due to direct emission of the gas, and ground-level ozone, a major component of urban smog, is produced by the photochemical reaction of nitrogen oxides (NO_x) and hydrocarbons (HC). Sulfur dioxides (SO_2) are emitted when the sulfur found in fuel is oxidized. As of 2007, on-road vehicles were estimated to be the single largest source for the major atmospheric pollutants, contributing 50% of the CO, 21% of the VOC's, 0.6% of SO_2, 7.0% of the NH_3 and 32% of the NO_x to the national emission inventory.[1]

Properly operating modern vehicles with three-way catalysts are capable of partially (or completely) converting engine-out CO, HC and NO_x emissions to carbon dioxide (CO_2), water and nitrogen. If there is a reducing environment on the catalyst, ammonia (NH_3) can be formed as a byproduct of the reduction of NO. For a complete description of the internal combustion engine and causes of pollutants in the exhaust see Heywood.[2]

NH_3, emitted from three-way catalyst equipped vehicles, is a growing concern because of the adverse health effects that have been attributed to its contribution to secondary particulate matter formation that is smaller than 2.5µm in diameter ($PM_{2.5}$).[3-5] Ammonium nitrate is known to be a dominate component of $PM_{2.5}$, though its NH_3 sources are commonly associated with livestock waste, fertilizer application, and sewage treatment.[6, 7] In urban areas these sources are less common and the contribution of ammonia from mobile sources is thought to be a significant and growing source.[6, 8] Its atmospheric levels are directly linked to the amount of free NH_3 in the atmosphere and with the recent reductions of sulfur from motor fuels this will have likely increased its availability.[6]

A direct knowledge of fleet averaged on-road emission levels is a critical input for estimating inventories, evaluating emission control programs and planning strategies that can lead to attaining National Ambient Air Quality Standards (NAAQS).[9] Many areas remain in non-attainment for the NAAQS, and with the 8 hour ozone standards introduced by the EPA in 1997, many locations still violating the standard may have great difficulty reaching attainment.[10] Knowing how tailpipe emission levels and their ratio's are changing in the on-road fleet requires monitoring programs that can collect enough measurements often enough to allow researchers to find and follow new trends.

The purpose of this report is to describe on-road emission measurements taken in three Californian cities in March of 2008, under Air Resources Board contract no. 07-319 that include measurements of SO_2, NH_3 and NO_2. Measurements were made on four consecutive days, March 4-7, at the on-ramp of the interchange from NB I-280 to NB I-880 in San Jose, CA. Measurements were previously collected at this site in 1999 for the California Inspection and Maintenance Review Committee (IMRC).[11] The second work site was at the interchange from 41N to 180W in Fresno, CA. Measurements were made for seven consecutive days from March 8-14. The final site, at the on-ramp from La Brea Blvd to I-10E in West L.A., was used for the

IMRC measurements in 1999 and for all of the Coordinating Research Council sponsored E-23 measurements in 2001, 2003, and 2005. The measurements were taken for five consecutive days, March 17-21.

MATERIALS AND METHODS

The remote sensor used in this study was developed at the University of Denver for measuring the pollutants in motor vehicle exhaust, and has previously been described in the literature.[12, 13] The instrument consists of a non-dispersive infrared (NDIR) component for detecting CO, CO_2, and HC, and twin dispersive ultraviolet (UV) spectrometer for measuring oxides of nitrogen (NO and NO_2), SO_2 and NH_3 (0.26 nm/diode resolution). The source and detector units are positioned on opposite sides of the road in a bi-static arrangement. Collinear beams of infrared (IR) and UV light are passed across the roadway into the IR detection unit, and are then focused onto a dichroic beam splitter, which serves to separate the beams into their IR and UV components. The IR light is then passed onto a spinning polygon mirror, which spreads the light across the four infrared detectors: CO, CO_2, HC and reference.

The UV light is reflected off of the surface of the dichroic mirror and is focused onto the end of a quartz fiber bundle that is mounted on the coaxial connector on the side of the detector unit. The quartz fiber bundle is split in order to carry the UV signal to two separate spectrometers. The first spectrometer was adapted to expand its UV range down to 200nm in order to measure the peaks from SO_2 and NH_3 and still measure the 227nm peak from NO. The absorbance from each respective UV spectrum of SO_2, NH_3, and NO is compared to a calibration spectrum using a classical least squares fitting routine in the same region in order to obtain the vehicle emissions. The second spectrometer measures only NO_2 by measuring an absorbance band at 438nm in the UV spectrum and comparing it to a calibration spectrum in the same region.[14]

The exhaust plume path length and density of the observed plume are highly variable from vehicle to vehicle, and are dependent upon, among other things, the height of the vehicle's exhaust pipe, wind, and turbulence behind the vehicle. For these reasons, the remote sensor only directly measures ratios of CO, HC, NO, SO_2, NH_3 or NO_2 to CO_2. The molar ratios of CO, HC, NO, SO_2, NH_3 or NO_2 to CO_2, termed Q^{CO}, Q^{HC}, Q^{NO}, Q^{SO2}, Q^{NH3} and Q^{NO2} respectively, are constant for a given exhaust plume, and on their own are useful parameters for describing a hydrocarbon combustion system. This study reports measured emissions as molar %CO, %HC, %NO, %SO_2, %NH_3 and %NO_2 in the exhaust gas, corrected for water and excess air not used in combustion. The HC measurement is calibrated with propane, a C_3 hydrocarbon. But based on measurements using flame ionization detection (FID) of gasoline vehicle exhaust, the remote sensor is only half as sensitive to exhaust hydrocarbons on a per carbon atom basis as it is to propane on a per carbon atom basis.[15] Thus, in order to calculate mass emissions as described below, the %HC values reported will first be multiplied by 2.0 as shown below, assuming that the fuel used is regular gasoline. These percent emissions can be directly converted into mass emissions by the equations shown below.

$$\text{gm CO/gallon} = 5506 \cdot \%CO / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1a)$$

$$\text{gm HC/gallon } = 2(8644 \cdot \%HC) / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1b)$$
$$\text{gm NO/gallon } = 5900 \cdot \%NO / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1c)$$
$$\text{gm SO}_2\text{/gallon} = 12{,}585 \cdot \%SO_2 / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1d)$$
$$\text{gm NH}_3\text{/gallon} = 3343 \cdot \%NH_3 / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1e)$$
$$\text{gm NO}_2\text{/gallon} = 9045 \cdot \%NO_2 / (15 + 0.285 \cdot \%CO + 2(2.87 \cdot \%HC)) \qquad (1f)$$

These equations indicate that the relationship between concentrations of emissions to mass of emissions is linear, especially for CO and NO and at low concentrations for HC. Thus, the percent difference in emissions calculated from the concentrations of pollutants reported here is equivalent to a difference calculated from masses. Note that NO is reported as grams of NO, while vehicle emission factors for NO_x are normally reported as grams of NO_2, even when the actual compound is NO.

Another useful conversion is from percent emissions to grams pollutant per kilogram (g/kg) of fuel. This conversion is achieved directly by first converting the pollutant ratio readings to moles of pollutant per mole of carbon in the exhaust using the following equation:

$$\frac{\text{moles pollutant}}{\text{moles C}} = \frac{\text{pollutant}}{CO + CO_2 + 6HC} = \frac{(\text{pollutant}/CO_2)}{(CO/CO_2) + 1 + 6(HC/CO_2)} = \frac{(Q^{CO}, 2Q^{HC}, Q^{NO} \ldots)}{Q^{CO} + 1 + 6Q^{HC}} \qquad (2)$$

Next, moles of pollutant are converted to grams by multiplying by molecular weight (e.g., 44 g/mole for HC since propane is measured), and the moles of carbon in the exhaust are converted to kilograms by multiplying (the denominator) by 0.014 kg of fuel per mole of carbon in fuel, assuming gasoline is stoichiometrically CH_2. Again, the HC/CO_2 ratio must use two times the reported HC (see above) because the equation depends upon carbon mass balance and the NDIR HC reading is about half a total carbon FID reading.[15]

$$\text{gm CO/kg } = (28Q^{CO} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3a)$$
$$\text{gm HC/kg } = (2(44Q^{HC}) / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3b)$$
$$\text{gm NO/kg } = (30Q^{NO} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3c)$$
$$\text{gm SO}_2\text{/kg} = (64Q^{SO2} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3d)$$
$$\text{gm NH}_3\text{/kg} = (17Q^{NH3} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3e)$$
$$\text{gm NO}_2\text{/kg} = (46Q^{NO2} / (1 + Q^{CO} + 6Q^{HC})) / 0.014 \qquad (3f)$$

Quality assurance calibrations are performed twice daily in the field unless observed voltage readings or meteorological changes are judged to warrant additional calibrations. For the multi-species instrument three calibration cylinders are needed. The first contains CO, CO_2, propane, NO and SO_2, the second contains NH_3 and propane and the final cylinder contains NO_2 and CO_2. A puff of gas is released into the instrument's path, and the measured ratios from the instrument are then compared to those certified by the cylinder manufacturer (Scott Specialty Gases). These calibrations account for day-to-day variations in instrument sensitivity and variations in ambient CO_2 levels caused by local sources, atmospheric pressure and instrument path length. Since propane is used to calibrate the instrument, all hydrocarbon measurements reported by the remote sensor are reported as propane equivalents.

Studies sponsored by the California Air Resources Board and General Motors Research Laboratories have shown that the remote sensor is capable of CO measurements that are correct to within ±5% of the values reported by an on-board gas analyzer, and within ±15% for HC.[16, 17] The NO channel used in this study has been extensively tested by the University of Denver, but we are still awaiting the opportunity to participate in an extensive blind study and instrument intercomparison to have it independently validated. Tests involving a late-model low-emitting vehicle indicate a detection limit (3σ) of 25 ppm for NO, with an error measurement of ±5% of the reading at higher concentrations.[13] Appendix A gives a list of criteria for determining valid or invalid data.

The remote sensor is accompanied by a video system to record a freeze-frame image of the license plate of each vehicle measured. The emissions information for the vehicle, as well as a time and date stamp, is also recorded on the video image. The images are stored digitally, so that license plate information may be incorporated into the emissions database during post-processing. A device to measure the speed and acceleration of vehicles driving past the remote sensor was also used in this study. The system consists of a pair of infrared emitters and detectors (Banner Industries) which generate a pair of infrared beams passing across the road, six feet apart and approximately two feet above the surface. Vehicle speed is calculated (reported to 0.1mph) from the time that passes between the front of the vehicle blocking the first and the second beam. To measure vehicle acceleration, a second speed is determined from the time that passes between the rear of the vehicle unblocking the first and the second beam. From these two speeds, and the time difference between the two speed measurements, acceleration is calculated (reported to 0.001 mph/sec). Appendix B defines the database format used for the data sets.

RESULTS FOR SAN JOSE

Measurements were made on four consecutive weekdays, from Monday, March 4, to Thursday, March 7, between the hours of 9:30 and 18:00 on the slightly uphill interchange ramp from NB I-280 to NB I-880. The instrument was located on an uphill portion of the ramp north of the I-280 to SB US 17 flyover. This was the same location used during the IMRC measurements in 1999. A satellite picture of the measurement location is shown in Figure 1 and a photograph of the setup is shown in Figure 2. The uphill grade at the measurement location averaged 1.8°. Appendix C gives temperature and humidity data for the 1999 and 2008 studies from the San Jose International Airport, approximately 3.5 miles north of the measurement site. Following the four days of data collection the images were read for license plate identification. Plates that appeared to be in state and readable were sent to the State of California to have the vehicle make and model year determined. The resulting database contained 24,978 records with make and model year information and valid measurements for at least CO and CO_2. Most of these records also contain valid measurements for HC, NO, SO_2, NH_3 and NO_2 as well. This and all previous databases can be found at www.feat.biochem.du.edu.

The validity of the attempted measurements is summarized in Table 1. The table describes the data reduction process beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration
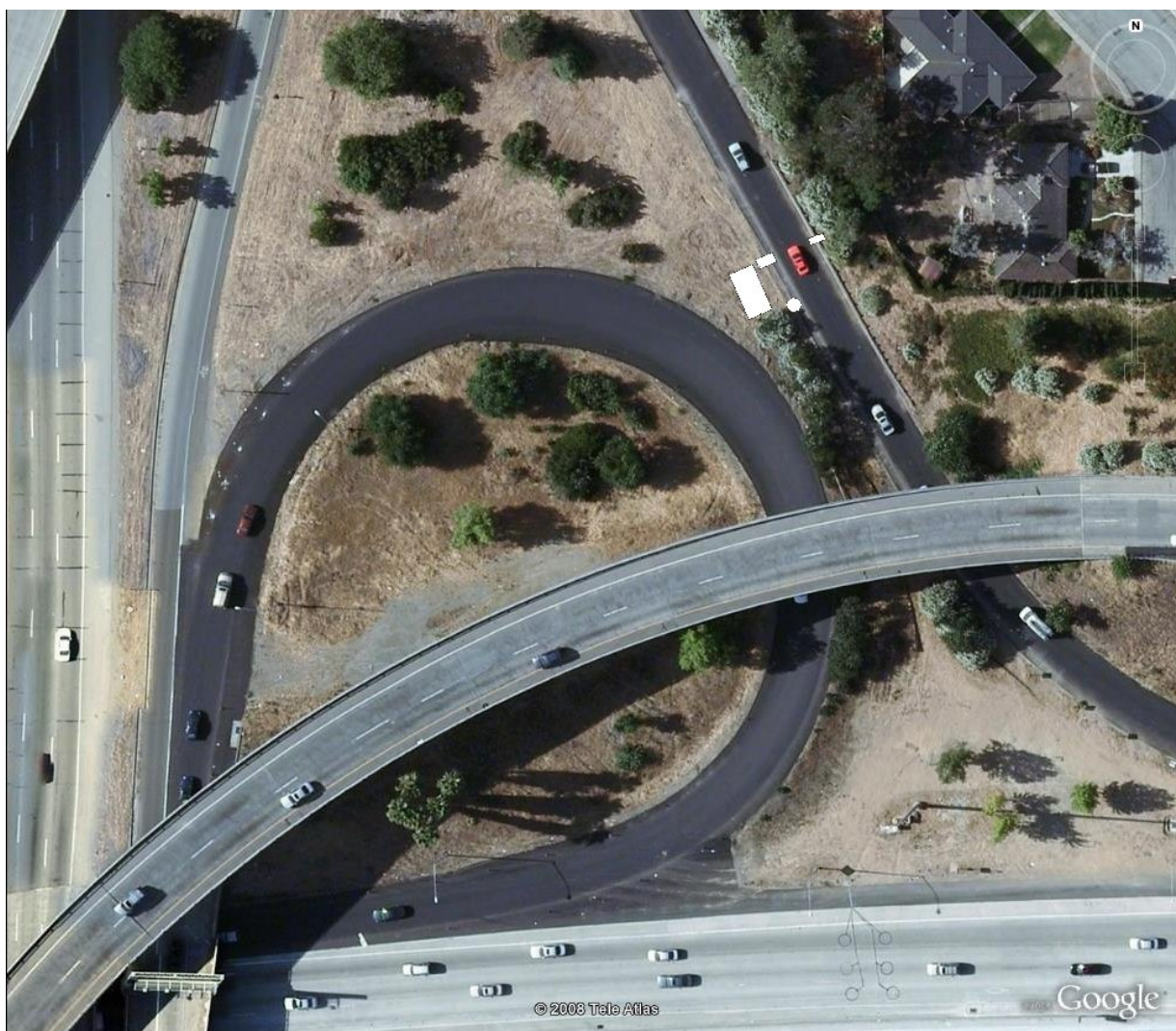
Figure 1. A satellite view of the San Jose interchange ramp from northbound I-280 to northbound I-880 with the approximate locations of the motor home (large rectangle), the remote sensing detector, source (small rectangles) and camera (circle).

Table 1. San Jose Validity Summary.

	CO	HC	NO	SO$_2$	NH$_3$	NO$_2$
Attempted Measurements	31,116					
Valid Measurements	27,567	27,567	27,567	27,562	27,566	27,500
Percent of Attempts	88.6%	88.6%	88.6%	88.6%	88.6%	88.4%
Submitted Plates	25,371	25,371	25,371	25,370	25,308	23,805
Percent of Attempts	81.5%	81.5%	81.5%	81.5%	81.3%	76.5%
Percent of Valid Measurements	92.0%	92.0%	92.0%	92.0%	91.8%	86.6%
Matched Plates	24,978	24,968	24,975	24,977	24,916	23,428
Percent of Attempts	80.3%	80.2%	80.3%	80.3%	80.1%	75.3%
Percent of Valid Measurements	90.6%	90.6%	90.6%	90.6%	90.4%	85.2%
Percent of Submitted Plates	98.5%	98.5%	98.5%	98.5%	98.5%	98.4%

Figure 2. The San Jose monitoring site showing the monitoring vehicle and the remote sensing detectors and speed and acceleration bars on the near side of the roadway.

information. An attempted measurement is defined as a beam block followed by a half second of data collection. If the data collection period is interrupted by another beam block from a closely following vehicle, the measurement attempt is aborted and an attempt is made at measuring the second vehicle. In this case, the beam block from the first vehicle is not recorded as an attempted measurement. Invalid measurement attempts arise when the vehicle plume is highly diluted, or the reported error in the ratio of the pollutant to CO_2 exceeds a preset limit (see Appendix A). The greatest loss of data in this process occurs during the plate reading process, when out-of-state vehicles and vehicles with unreadable plates (obscured, missing, dealer, out of camera field of view etc.) are omitted from the final database.

Table 2 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 24,978 records used in this fleet analysis, 18,354 (73.5%) were contributed by vehicles measured once, and the remaining 6,624 (26.5%) records were from vehicles measured at least twice. Table 3 is the historic data summary; included are summaries of the previous remote sensing databases collected at the San Jose site. The other measurements were conducted in October of 1999. The average HC values here have been adjusted to remove a systematic offset in the HC measurements. This offset, restricted to the HC

Table 2. San Jose number of measurements of repeat San Jose vehicles.

Number of Times	Number of Vehicles	Percent of Measurements
1	18,354	73.5%
2	2,210	17.7%
3	533	6.4%
4	125	2.0%
5	15	0.3%
6	5	0.1%

channel and reported earlier in the CRC E-23 program, is evident in the lowest emitting HC vehicles.[18] Calculation of the offset is accomplished by computing the mode and means of the newest model year vehicles, and assuming that these vehicles emit negligible levels of hydrocarbons then we use the lowest of either of these values as the offset. The offset adjustment subtracts or adds this value from all of the hydrocarbon data. Since we assume the cleanest vehicles to emit little hydrocarbons, such an approximation will only err slightly towards clean because the true offset will be a value somewhat less than the average of the cleanest model year and make. This adjustment facilitates comparisons with the other E-23 sites and/or different collection years for the same site. The offset has been applied where indicated in the analyses in this report, but has not been applied to the archived database.

Mean fleet emissions for CO, HC and NO have decreased dramatically between 1999 and 2008. These large reductions have been reported at other sites in the US and these reductions (CO -66%, HC -74% and NO -40%) are consistent with those reported.[19] These reductions have occurred despite the average age of the measured fleet increasing by about 1.5 model years. Average speeds and accelerations were higher in the 1999 data set and might reflect less congestion.

Figure 3 graphs the relationship between vehicle emissions of CO, HC and NO and model year for the two data sets that have been collected at this site. The HC data have been offset adjusted as previously describe for the purpose of comparison. The HC data are the only data that does not show positive emissions deterioration for the vehicles between the 1999 and 2008 data sets. This may be a result of the lower average speed observed in 2008 (30.6 mph vs. 33.2 mph) precluding fewer decelerations that can result in elevated HC emissions. Figure 4 is the same plot for the new emissions species of SO_2, NH_3 and NO_2 that were collected for the first time with the 2008 measurements. SO_2 and NH_3 show a model year dependence while NO_2 does not appear to have one.

As originally shown by Ashbaugh et al.,[17] vehicle emissions by model year, with each model year divided into emission quintiles, were plotted for data collected in 2008. This resulted in the plots shown in Figures 5 - 7. The bars represent the mean emissions for each quintile, and do not account for the number of vehicles in each model year. This figure illustrates that the cleanest 60% of the vehicles, regardless of model year, make an essentially negligible contribution to the total fleet emissions. The large accumulations of negative emissions in the first two quintiles are the result of ever decreasing emission levels. Our instrument is designed such that when measuring a true zero emission plume, half of the readings will be negative and half will be

Table 3. San Jose Historic Data Summary.

Study Year	1999	2008
Mean CO (%) (g/kg of fuel)	0.4 (48.5)	0.13 (16.6)
Median CO (%)	0.07	0.02
Percent of Total CO from Dirtiest 10% of the Fleet	73.4%	82.4%
Mean HC (ppm)* (g/kg of fuel)* Offset (ppm)	151 (5.7) 10	38 (1.5) 30
Median HC (ppm)*	90	10
Percent of Total HC from Dirtiest 10% of the Fleet	72.1%	55.3%
Mean NO (ppm) (g/kg of fuel)	312 (4.3)	186 (2.6)
Median NO (ppm)	100	29
Percent of Total NO from Dirtiest 10% of the Fleet	57.5%	67.8%
Mean SO_2 (ppm) (g/kg of fuel)	NA	2 (0.06)
Median SO_2 (ppm)	NA	0.6
Percent of Total SO_2 from Dirtiest 10% of the Fleet	NA	74.9%
Mean NH_3 (ppm) (g/kg of fuel)	NA	61 (0.5)
Median NH_3 (ppm)	NA	16
Percent of Total NH_3 from Dirtiest 10% of the Fleet	NA	58.3%
Mean NO_2 (ppm) (g/kg of fuel)	NA	2 (0.05)
Median NO_2 (ppm)	NA	0.6
Percent of Total NO_2 from Dirtiest 10% of the Fleet	NA	60.5%
Mean Model Year	1992.8	2000.6
Mean Speed (mph)	33.2	30.6
Mean Acceleration (mph/s)	1.3	1.0
Mean VSP (kw/tonne) Slope (degrees)	18.7 1.8°	14.7 1.8°
*Indicates values that have been HC offset adjusted as described in text.		
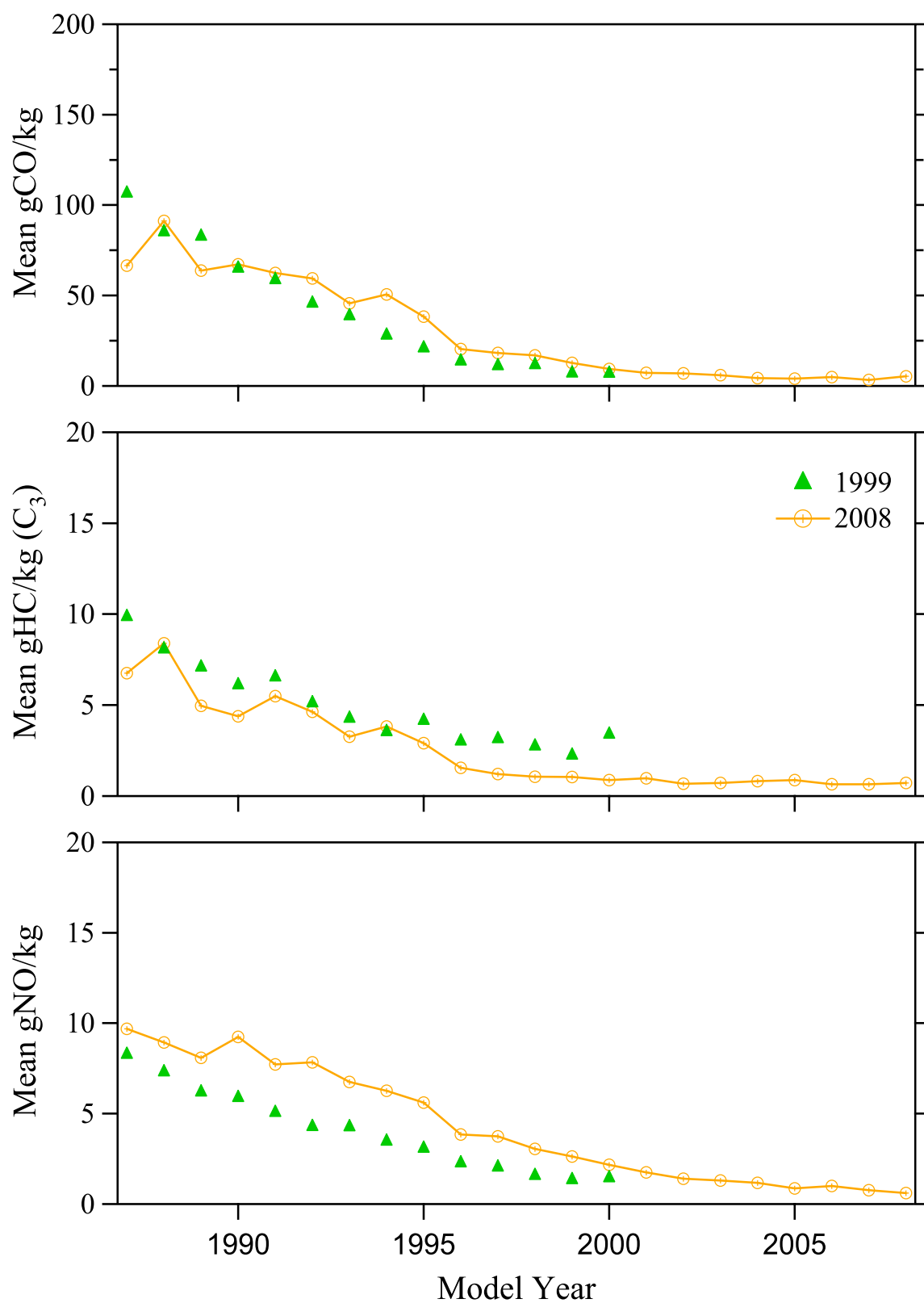
Figure 3. San Jose mean vehicle emissions illustrated as a function of model year. HC data have been offset adjusted as described in the text.
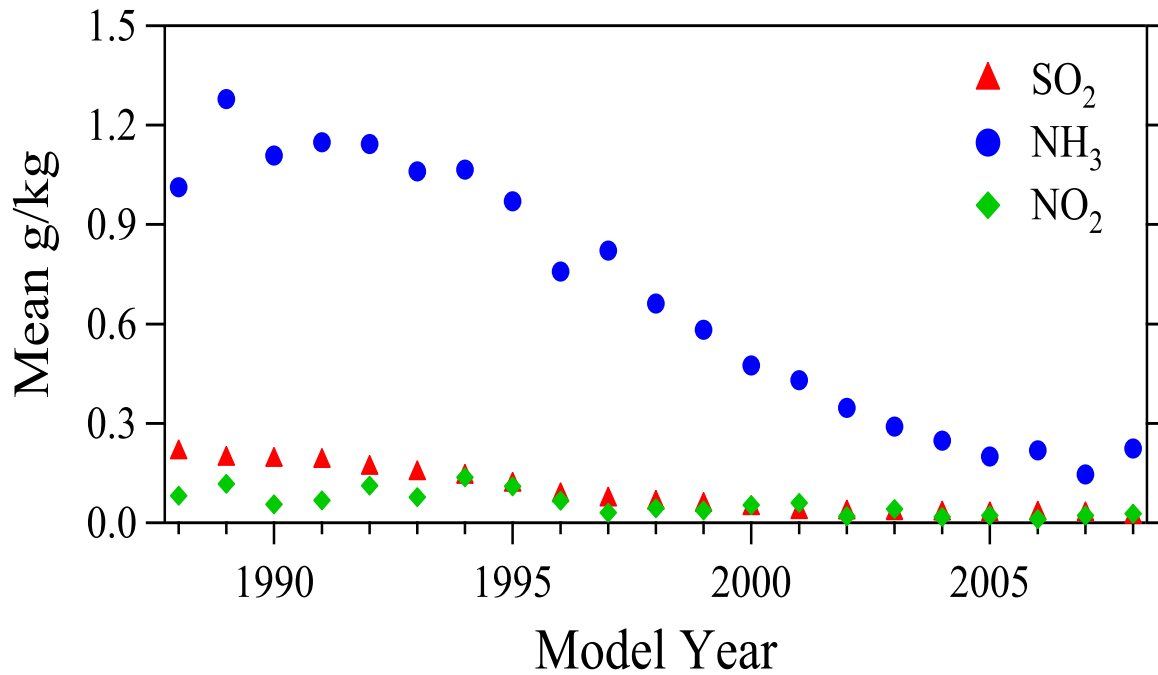
Figure 4. SO$_2$, NH$_3$ and NO$_2$ mean vehicle emissions of as a function of model year for the 2008 San Jose measurements. All new species comparison graphs are plotted on the same scale for all sites for ease of comparison.

positive. As the lowest emitting segments of the fleets continue to dive toward zero emissions, the negative emission readings will continue to grow toward half of the measurements.

Figures 5 - 7 can also be used to get a picture of federal compliance standards. The on-road data are measured as mass emissions per kg of fuel. It is not possible to determine mass emissions per mile for each vehicle because the instantaneous gasoline consumption (kg/mile) is not known. An approximate comparison with the fleet average emissions shown in Figures 5 - 7 can, however, be carried out. To make this comparison, we assume a fuel density of 0.75 kg/L and an average gas mileage for all model years of 23mpg. The Tier 1, 100,000 mile standards for CO, HC, and NO are 4.2, 0.31, and 0.6 gm/mi, respectively.[20] With the above assumptions, these correspond to 34, 2.5, and 4.9 gm/kg, respectively. Inspection of Figures 5 - 7 shows that significant fractions, especially of the newer vehicles, are measured with on-road emissions well below these standards. One additional observation can be made from the middle graph of the fleet fraction as a function of model year. At the San Jose site the 2001 – 2002 recession is clearly visible with a drop in new car sales after the 2001 model year that bottomed out with the 2003 model year and then recovered.

An equation for determining the instantaneous power of an on-road vehicle has been proposed by Jimenez,[21] which takes the form

$$VSP = 4.39 \cdot \sin(slope) \cdot v + 0.22 \cdot v \cdot a + 0.0954 \cdot v + 0.0000272 \cdot v^3 \quad (4)$$

where VSP is the vehicle specific power in kW/metric tonne, *slope* is the slope of the roadway (in degrees), *v* is vehicle speed in mph, and *a* is vehicle acceleration in mph/s. Derived from

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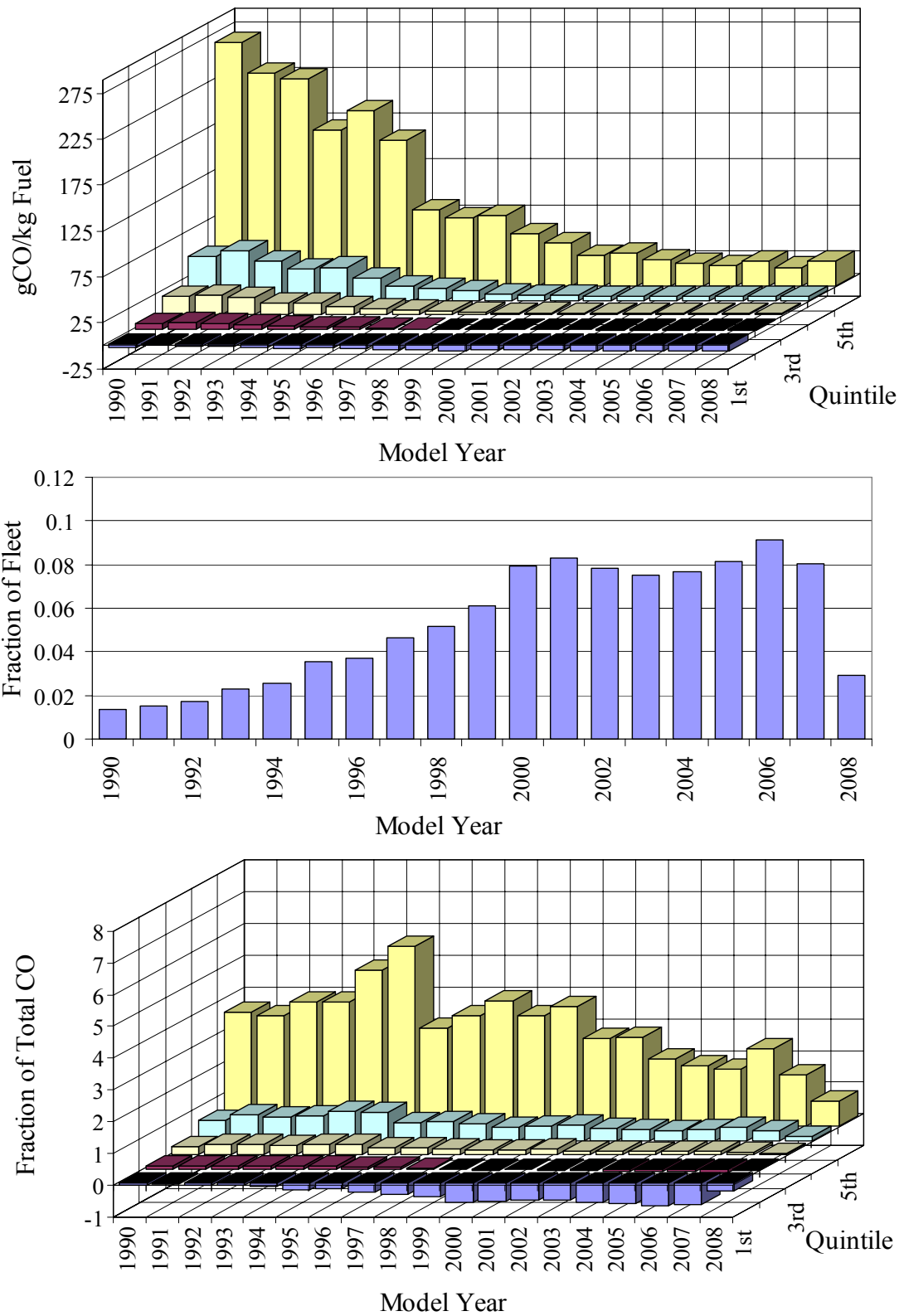
Figure 5. 2008 San Jose CO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional CO emissions by model year and quintile (bottom).
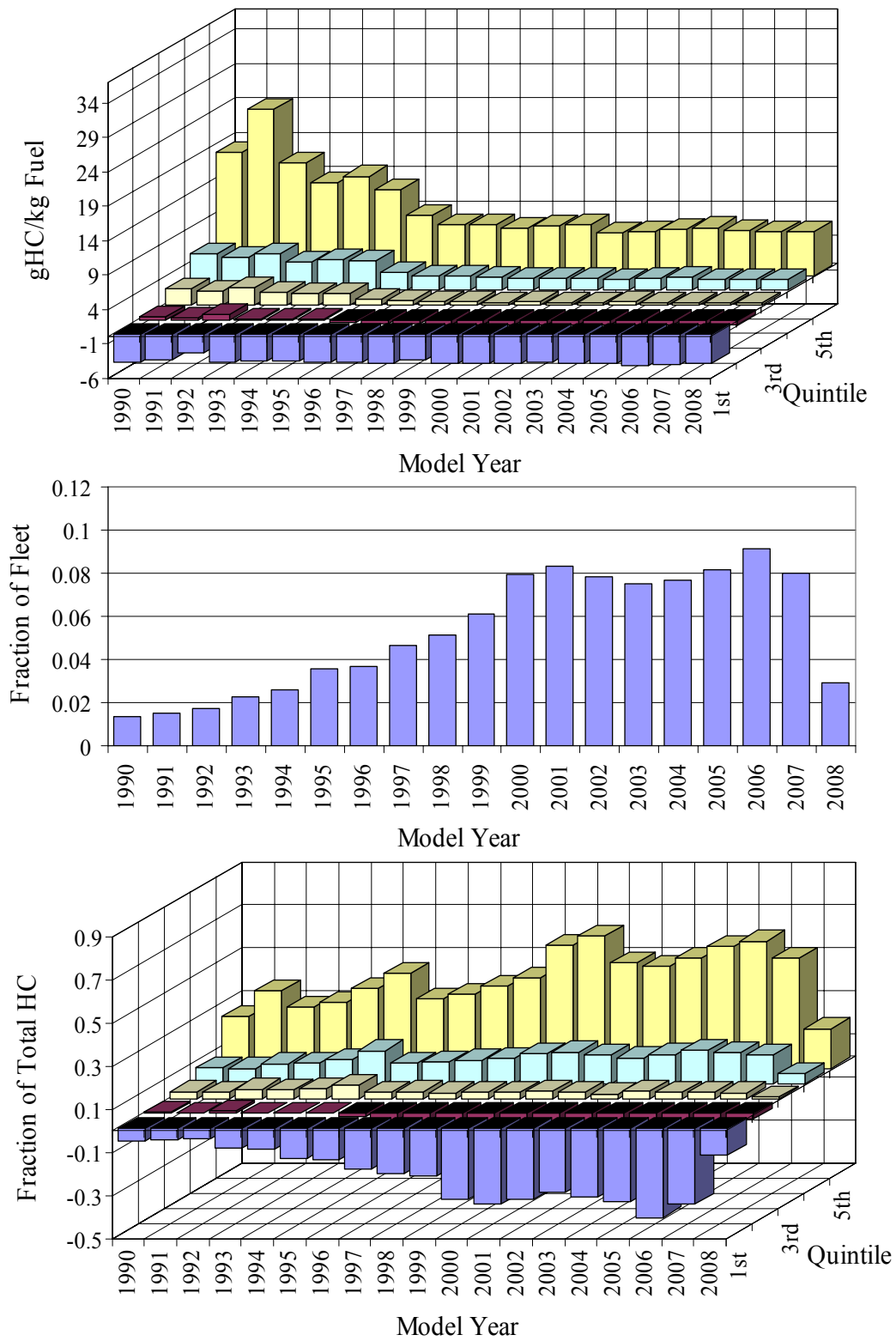
Figure 6. 2008 San Jose HC emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional HC emissions by model year and quintile (bottom).
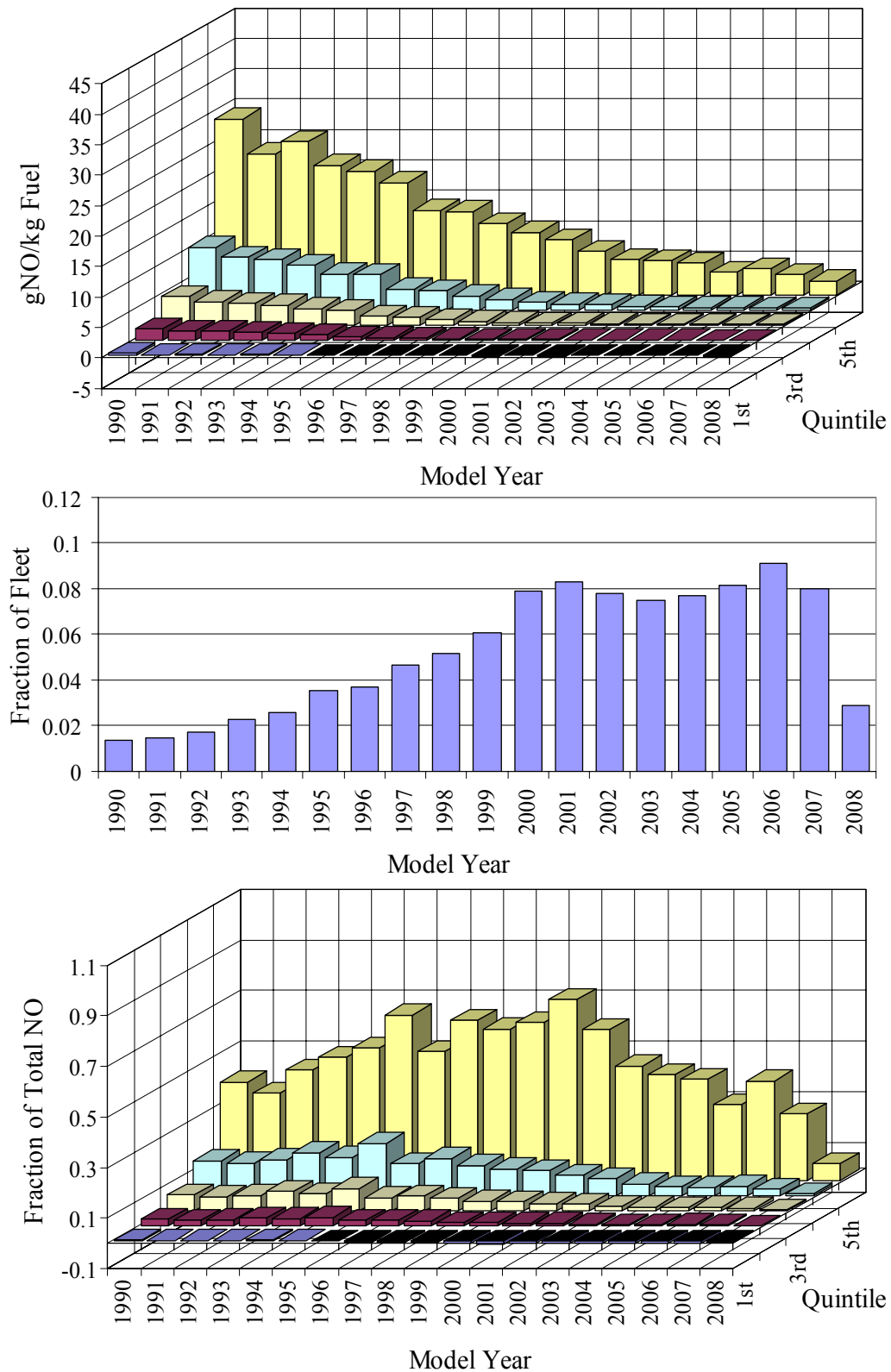
Figure 7. 2008 San Jose NO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional NO emissions by model year and quintile (bottom).

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dynamometer studies, and necessarily an approximation, the first term represents the work required to climb the gradient, the second term is the $f = ma$ work to accelerate the vehicle, the third is an estimated friction term, and the fourth term represents aerodynamic resistance. Using this equation, VSP was calculated for all measurements in each year's databases. This equation, in common with all dynamometer studies, does not include any load effects arising from road curvature. The emissions data were binned according to vehicle specific power, and illustrated in Figure 8. All of the specific power bins contain at least 400 measurements. The HC data have been offset adjusted for this comparison.

Because of the nine year difference between the two data sets a large emissions decrease for each species has been observed. The HC emissions continue to show a negative dependence on specific power however all of the primary emissions show less dependence on VSP. The error bars included in the plot are standard errors of the mean calculated from the daily averages. These uncertainties were generated for these γ-distributed data sets by applying the central limit theorem. Each day's average emissions for a given VSP bin were assumed an independent measurement of the emissions at that VSP. Normal statistics were then applied to these daily averages.

Figure 9 is a simlar plot of the emissions of SO_2, NH_3 and NO_2 as a function of vehicle specific power for the 2008 measurements. The NH_3 error bars included in the plot are standard errors of the mean calculated from the daily averages. NH_3 is the only species to show any dependence on driving mode with a positive dependence on specific power.

In the manner described in the CRC E-23 Phoenix, Year 2 report,[22] instrument noise was measured using the slope of the negative portion of a plot of the natural log of the binned emission measurement frequency versus the emission level. Such plots were constructed for all the species measured. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor, which describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors were 5.2, 2.8, 0.3, 0.04, 0.006 and 0.3 for CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These values indicate standard deviations of 7.3 g/kg (0.06%), 4.0 g/kg (95ppm), 0.4 g/kg (30ppm), 0.06 g/kg (2ppm), 0.009 g/kg (2ppm) and 0.4 g/kg (38ppm) for individual measurements of CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These levels are consistent with the low noise level.[22] In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per bin, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages of 100 measurements reduce to 0.7 g/kg, 0.4 g/kg, 0.04 g/kg, 0.006 g/kg, 0.0009 g/kg and 0.04 g/kg, respectively.
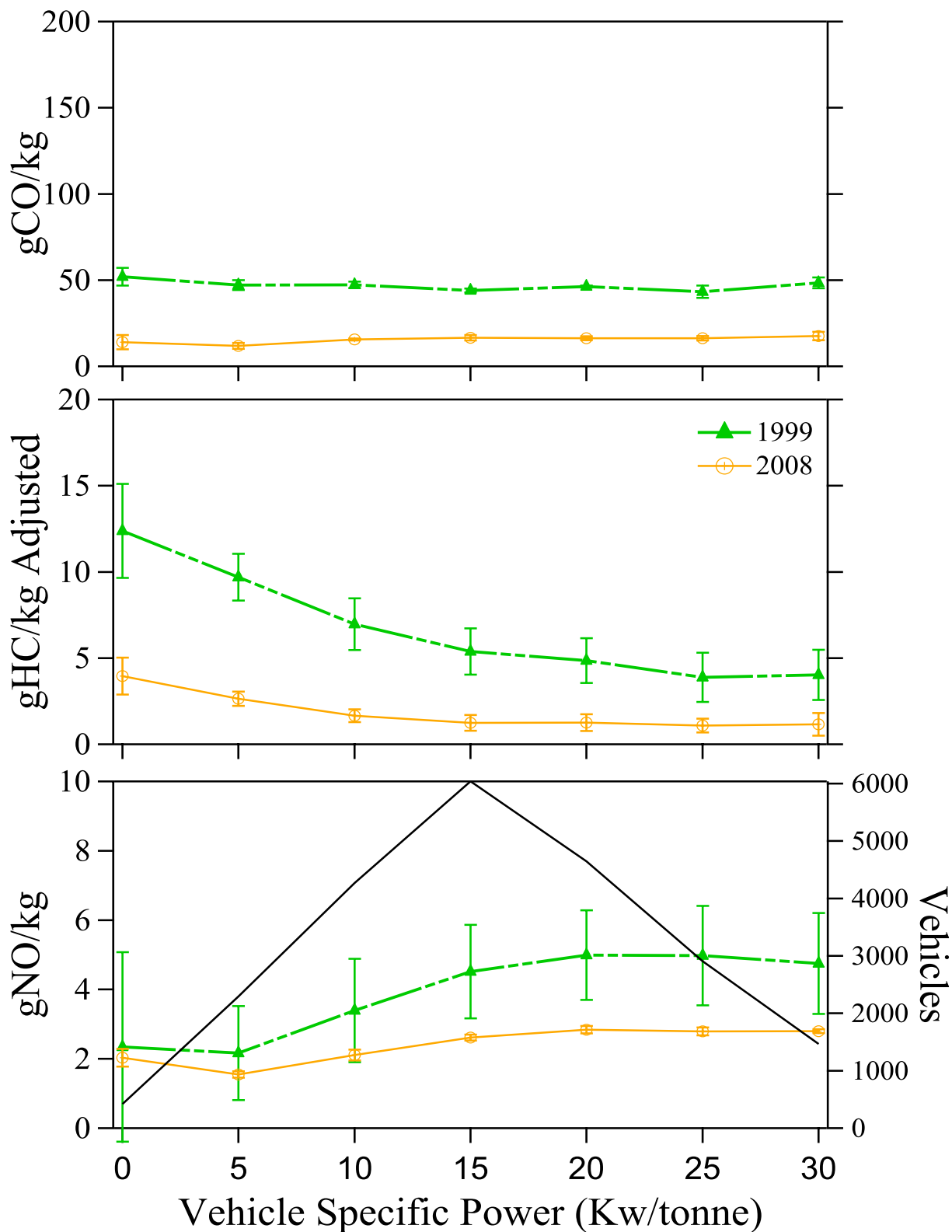
Figure 8. Vehicle emissions as a function of vehicle specific power for the San Jose data sets with valid speed and acceleration measurements. Error bars are standard errors of the mean calculated from daily samples and the solid line in the bottom graph is the number of vehicles in each bin for the 2008 data.
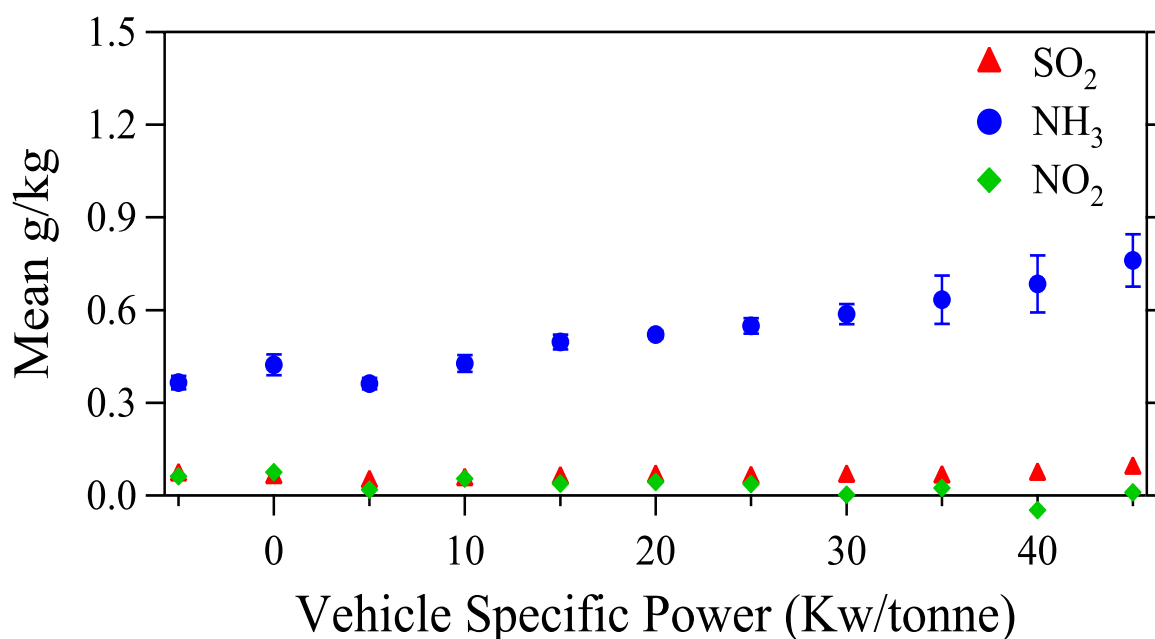
Figure 9. SO_2, NH_3 and NO_2 emissions as a function of vehicle specific power for the 2008 San Jose data with valid speed and acceleration measurements. The NH_3 error bars are standard errors of the mean calculated from daily samples. All new species comparison graphs are plotted on the same scale for all sites for ease of comparison.

RESULTS FOR FRESNO

Measurements were made on seven consecutive days, from Saturday, March 8, to Friday, March 14, between the hours of 7:30 and 19:00 on the uphill interchange ramp from NB US 41 to WB US 180. The instrument was located on an uphill portion of the ramp and these are the first measurements we have ever collected in the Fresno area. A satellite photo of the measurement location is shown in Figure 10 and a photograph of the setup is shown in Figure 11. The uphill grade at the measurement location averaged 1.8°. Appendix C provides the temperature and humidity data for the 2008 studies from the Fresno Yosemite International Airport, approximately 3.25 miles northeast of the measurement site. Following the seven days of data collection the images were read for license plate identification. Plates that appeared to be in state and readable were sent to the State of California to have the vehicle make and model year determined. The resulting database contained 13,365 records with make and model year information and valid measurements for at least CO and CO_2. Most of these records also contain valid measurements for HC, NO, SO_2, NH_3 and NO_2 as well. This and all previous databases can be found at www.feat.biochem.du.edu.

The validity of the attempted measurements is summarized in Table 4. The table describes the data reduction process beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration information. A complete description of the process has been provided in the San Jose results section and the measurement error rejection criteria are provided in Appendix A.
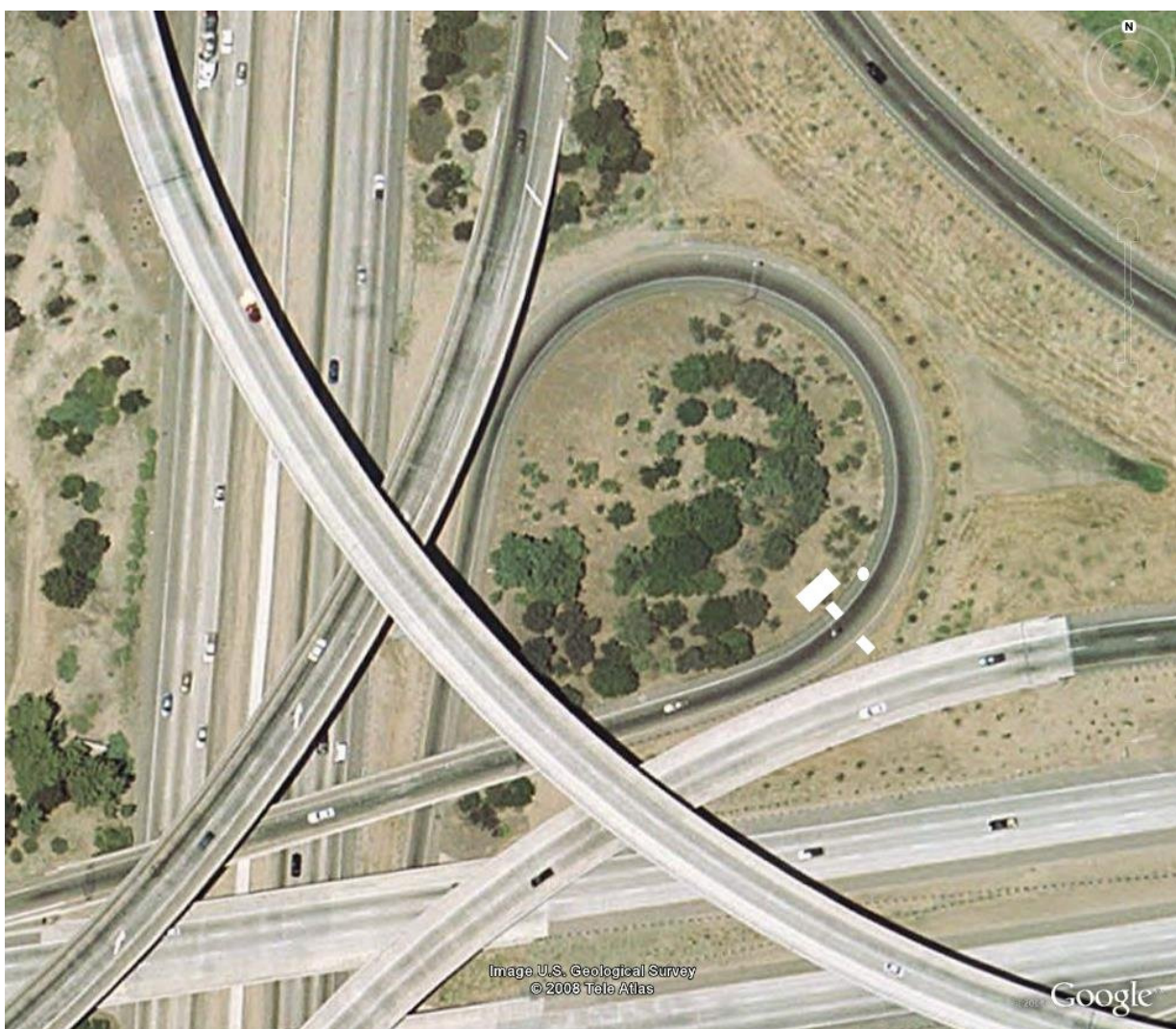
Figure 10. A satellite view of the Fresno interchange ramp from northbound US 41 to westbound US 180 with the approximate locations of the motor home (large rectangle), the remote sensing detector, source (small rectangles) and camera (circle).

Table 4. Fresno Validity Summary.

	CO	HC	NO	SO_2	NH_3	NO_2
Attempted Measurements	15,656					
Valid Measurements	15,048	15,048	15,006	15,045	15,046	15,024
Percent of Attempts	96.1%	96.1%	95.8%	96.1%	96.1%	96.0%
Submitted Plates	13,679	13,641	13,678	13,677	13,661	13,327
Percent of Attempts	87.4%	87.1%	87.4%	87.4%	87.3%	85.1%
Percent of Valid Measurements	90.9%	90.6%	91.2%	90.9%	90.8%	88.7%
Matched Plates	13,365	13,329	13,364	13,363	13,349	13,025
Percent of Attempts	85.4%	85.1%	85.4%	85.4%	85.3%	83.2%
Percent of Valid Measurements	88.9%	88.6%	89.1%	88.9%	88.8%	86.7%
Percent of Submitted Plates	97.8%	97.8%	97.8%	97.8%	97.8%	97.8%

Figure 11. The Fresno monitoring site showing the monitoring vehicle and the remote sensing detectors and speed and acceleration bars.

Table 5 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 13,365 records used in this fleet analysis, 7,875 (58.9%) were contributed by vehicles measured once, and the remaining 5,490 (41.1%) records were from vehicles measured at least twice.

Table 5. Fresno number of measurements of repeat vehicles.

Number of Times	Number of Vehicles	Percent of Measurements
1	7875	58.9%
2	1157	17.3%
3	463	10.4%
4	203	6.1%
5	100	3.7%
6	47	2.1%
7	14	0.8%
>7	11	0.7%

Table 6 provides a summary of the measurements collected in Fresno. Since this is the first remote sensing data to have been collected in the Fresno area there are no previous

Table 6. Fresno Data Summary.

Study Year	2008
Mean CO (%)	0.16
(g/kg of fuel)	(20.0)
Median CO (%)	0.02
Percent of Total CO from Dirtiest 10% of the Fleet	80.8%
Mean HC (ppm)*	72
(g/kg of fuel)*	(2.9)
Offset (ppm)	30
Median HC (ppm)*	40
Percent of Total HC from Dirtiest 10% of the Fleet	50.4%
Mean NO (ppm)	202
(g/kg of fuel)	(2.9)
Median NO (ppm)	12
Percent of Total NO from Dirtiest 10% of the Fleet	70.2%
Mean SO_2 (ppm)	3
(g/kg of fuel)	(0.09)
Median SO_2 (ppm)	0.8
Percent of Total SO_2 from Dirtiest 10% of the Fleet	71.4%
Mean NH_3 (ppm)	62
(g/kg of fuel)	(0.5)
Median NH_3 (ppm)	21
Percent of Total NH_3 from Dirtiest 10% of the Fleet	53.2%
Mean NO_2 (ppm)	7
(g/kg of fuel)	(0.14)
Median NO_2 (ppm)	3.5
Percent of Total NO_2 from Dirtiest 10% of the Fleet	91.4%
Mean Model Year	1999.8
Mean Speed (mph)	25.4
Mean Acceleration (mph/s)	0
Mean VSP (kw/tonne)	6.4
Slope (degrees)	1.8°
*Indicates values that have been HC offset adjusted as described in text.	

measurements to compare with. The average HC values have been offset adjusted as previously described to remove an artificial offset in the measurements. The fleet at this location in Fresno is more than three-quarters of a model year older than that measured in San Jose and 1.4 model years older than the fleet from west Los Angeles. The emissions of CO, HC and NO are similar to those observed at the other two sites. In addition the fraction of HC emissions that the dirtiest 10% of the fleet is responsible for is similar to the lighter driving loads seen at the San Jose site.

Figure 12 shows the emissions versus model year plot for the Fresno data. More noise is evident due to the smaller data set but similar trends for the three primary pollutants are seen. The HC data are offset adjusted as previously described and the y-axis ranges for each pollutant have been held in common for all three sites for comparison purposes. Figure 13 is the same plot for SO_2, NH_3 and NO_2 that were collected for the first time with the 2008 measurements. SO_2 and NH_3 shows a model year dependence, increasing with age, while NO_2 shows no model year dependence but does have a very large spike in emissions in the 2007 model year (see discussion for more details).

Figures 14 – 16 are plots of the Fresno vehicle emissions by model year, with each model year divided into emission quintiles. The bars represent the mean emissions for each quintile, and do not account for the number of vehicles in each model year. As seen in these plots at the San Jose site the cleanest 60% of the vehicles, regardless of model year, make a negligible contribution to the total fleet emissions. In addition the Tier 1 cut-points of 34, 2.5 and 4.9 gm/kg of CO, HC and NO show that significant fractions of vehicles in Fresno are measured below these levels.[20] Comparing the fleet fractions versus model year plots with the San Jose data shows that the recession in 2001 – 2002 has had a more lasting effect at the Fresno site. The plot shows that new car sales in the Fresno areas that this site reaches into have never recovered compared with the San Jose site where sales rebounded with the 2004 model year.

Figure 17 uses equation (4) to calculate the vehicle specific power in kW/metric tonne and plot the results. Because the traffic density is very low at this location the observed driving mode is lightly loaded and that is reflected in the emission graphs. All of the specific power bins contain at least 67 measurements. The HC data have been offset adjusted for this comparison. The error bars included in the plot are standard errors of the mean calculated from the daily averages.

Figure 18 is the plot of the emissions of SO_2, NH_3 and NO_2 as a function of vehicle specific power for the 2008 measurements. The NH_3 error bars included in the plot are standard errors of the mean calculated from the daily averages. NH_3 is the only species to show any dependence on driving mode with a positive dependence on specific power despite the lighter loads at the Fresno site.

Instrument noise was measured using the slope of the negative portion of a plot of the natural log of the binned emission measurement frequency versus the emission level. Such plots were constructed for the three primary pollutants. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor, which describes the noise present in the
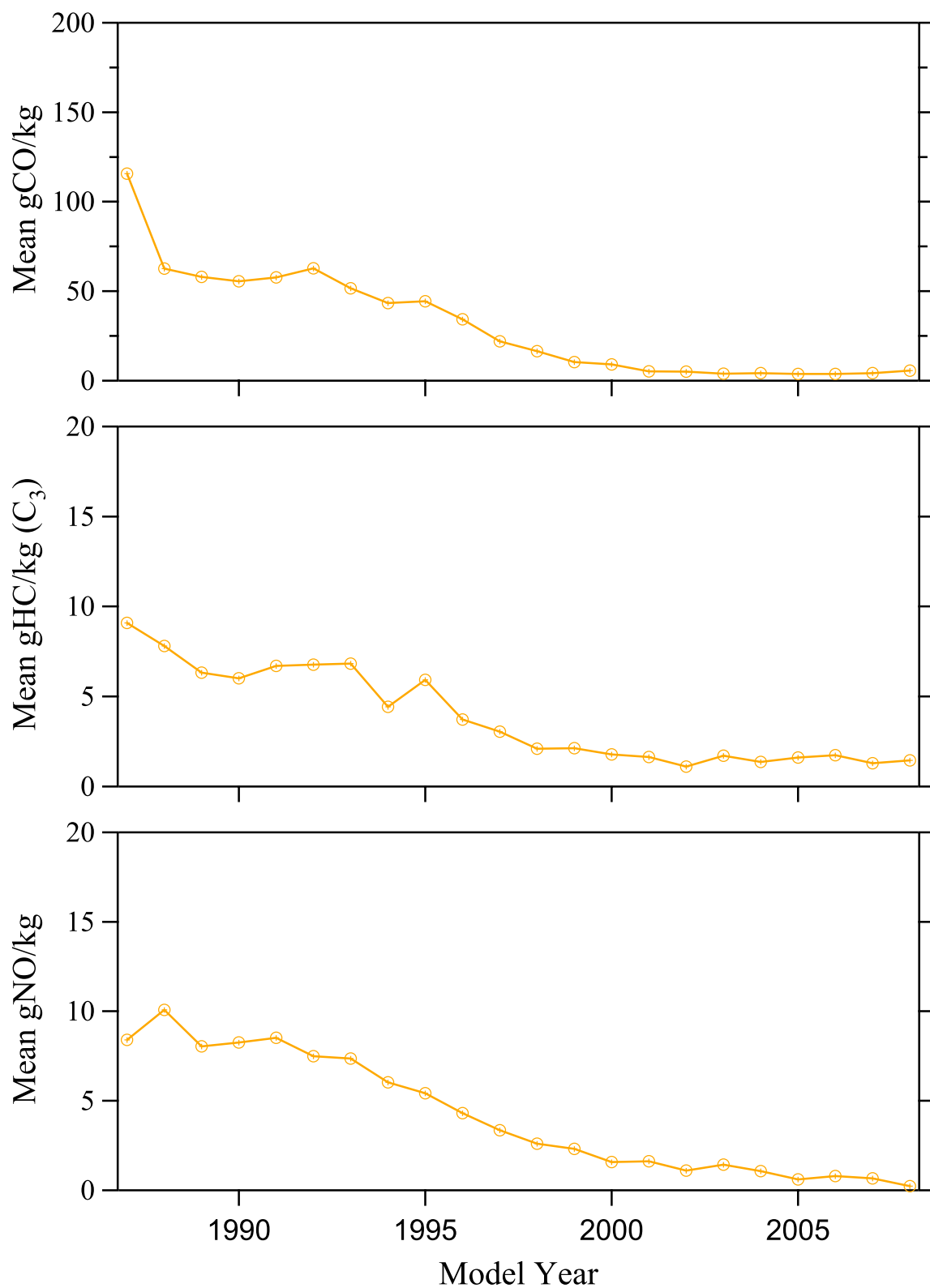
Figure 12. Fresno 2008 mean vehicle emissions illustrated as a function of model year. HC data have been offset adjusted as described in the text.
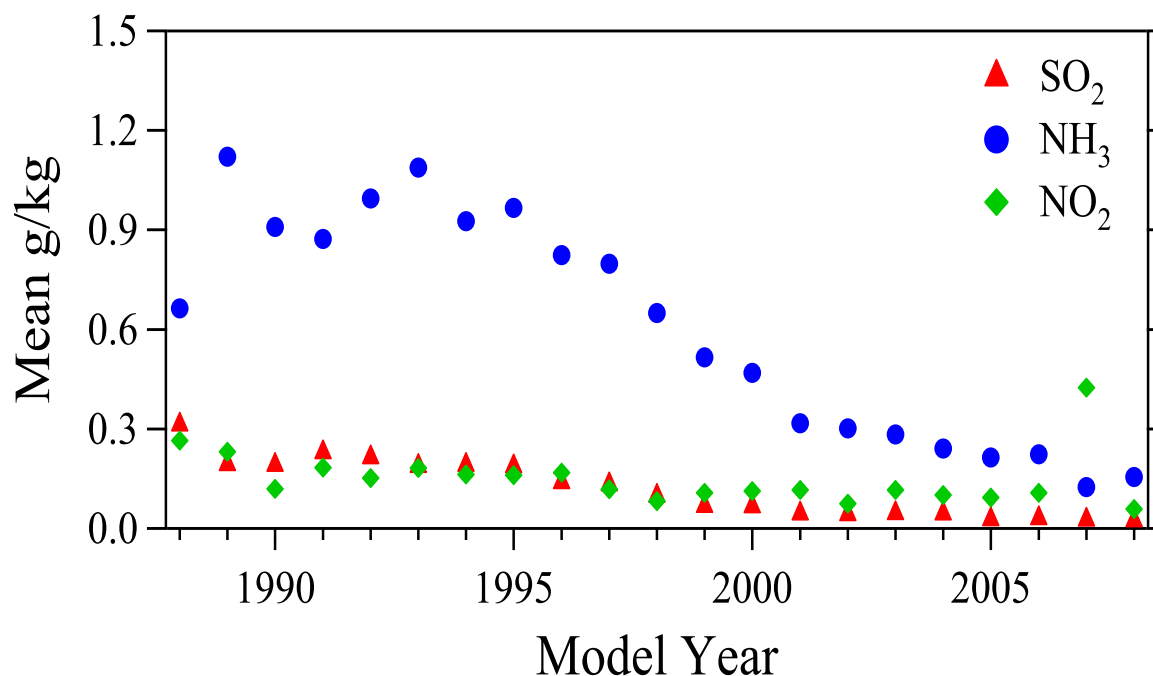
Figure 13. SO_2, NH_3 and NO_2 mean vehicle emissions of as a function of model year for the 2008 Fresno measurements.

measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors were 3.8, 3.0, 0.1, 0.04, 0.01 and 0.2 for CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These values indicate standard deviations of 3.8 g/kg (0.04%), 4.3 g/kg (103ppm), 0.2 g/kg (15ppm), 0.06 g/kg (2ppm), 0.02 (2ppm) and 0.3 g/kg (15ppm) for individual measurements of CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These levels are consistent with the low noise level as discussed in a previous Phoenix report.[22] In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per bin, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages of 100 measurements reduce to 0.4 g/kg, 0.4 g/kg, 0.02 g/kg, 0.006 g/kg, 0.002 g/kg and 0.03 g/kg, respectively.
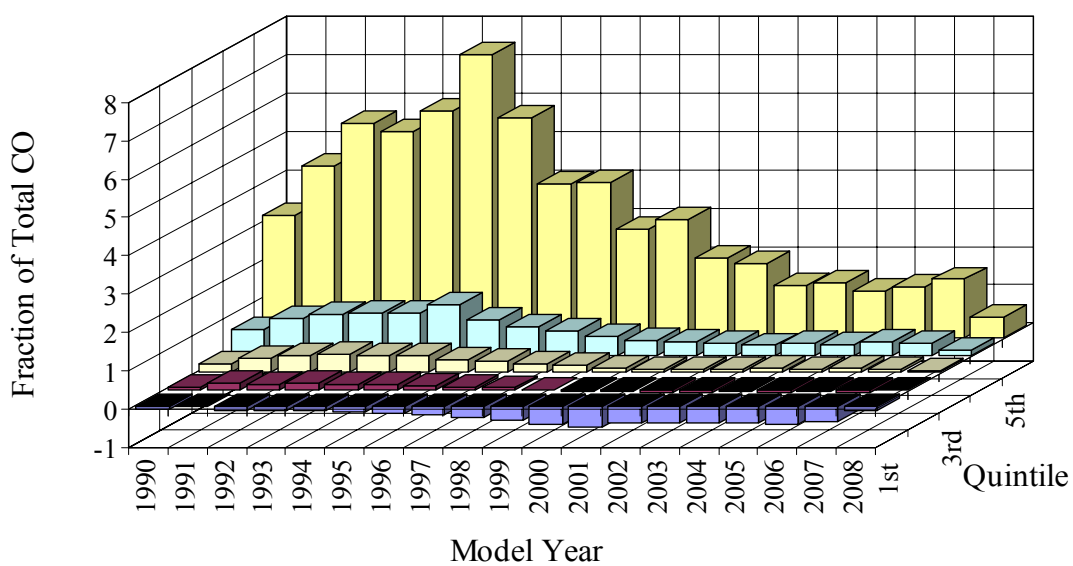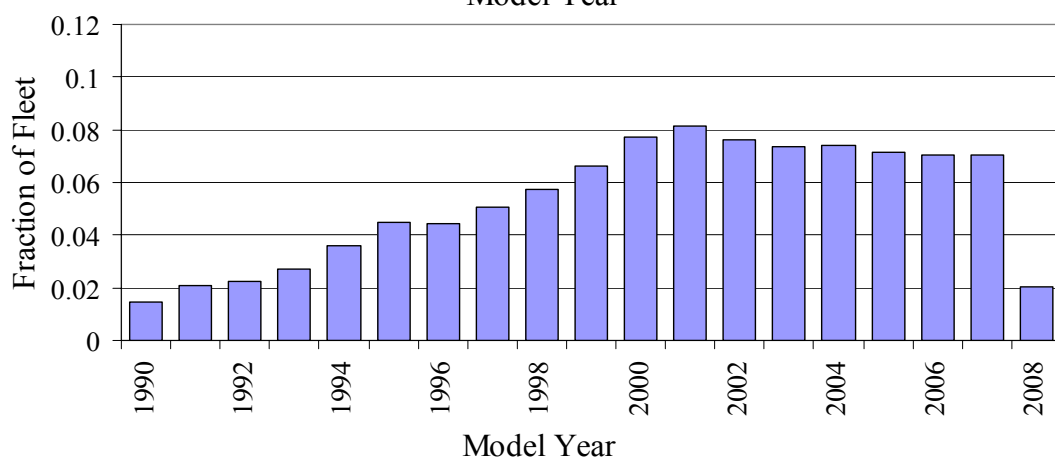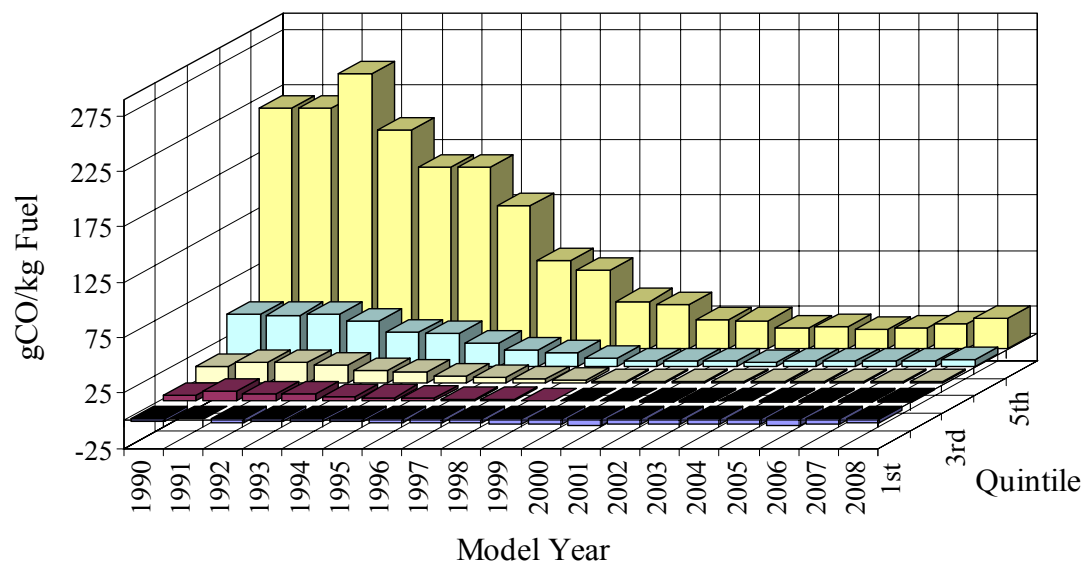
Figure 14. 2008 Fresno CO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional CO emissions by model year and quintile (bottom).
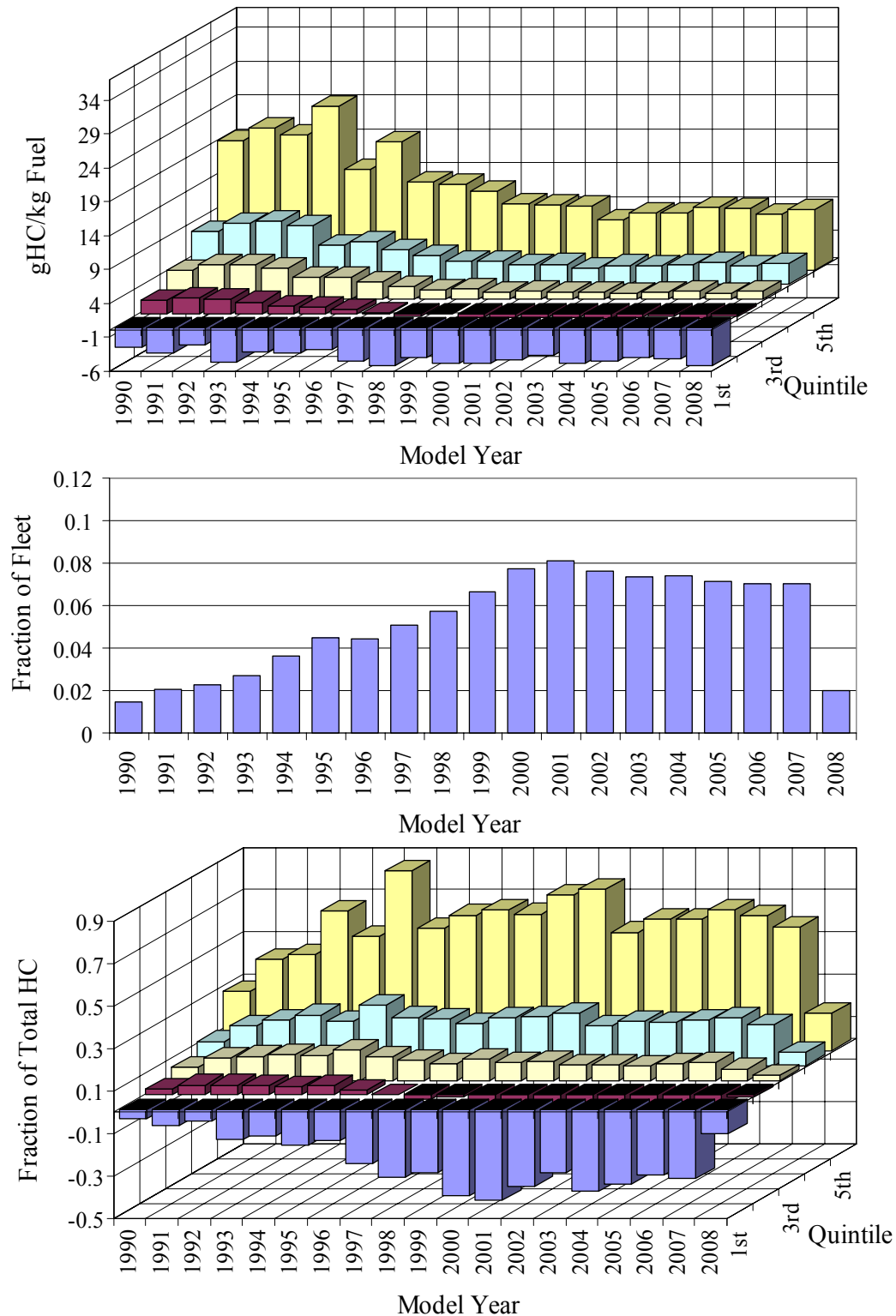
Figure 15. 2008 Fresno HC emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional HC emissions by model year and quintile (bottom).
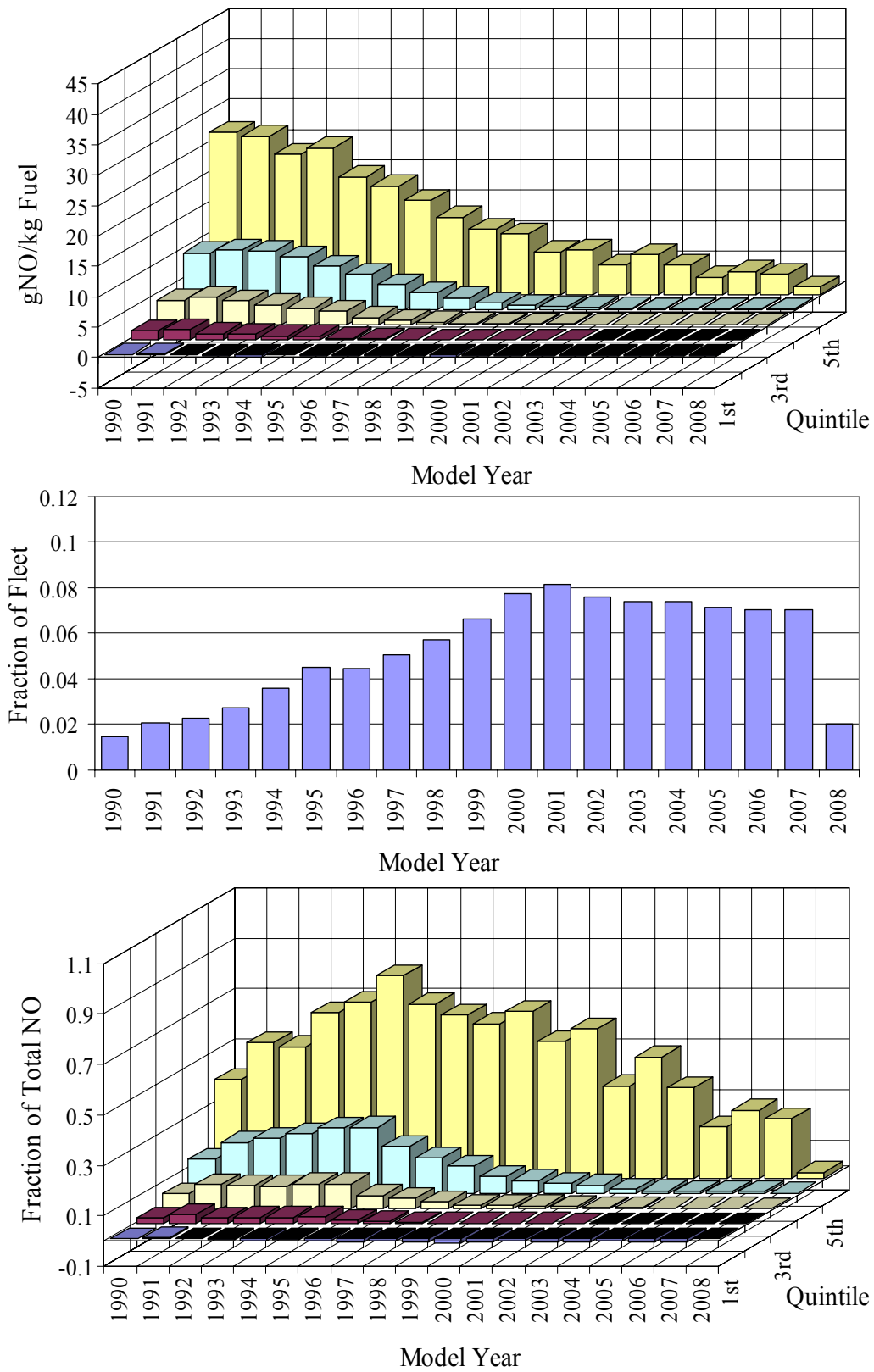
Figure 16. 2008 Fresno NO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional NO emissions by model year and quintile (bottom).
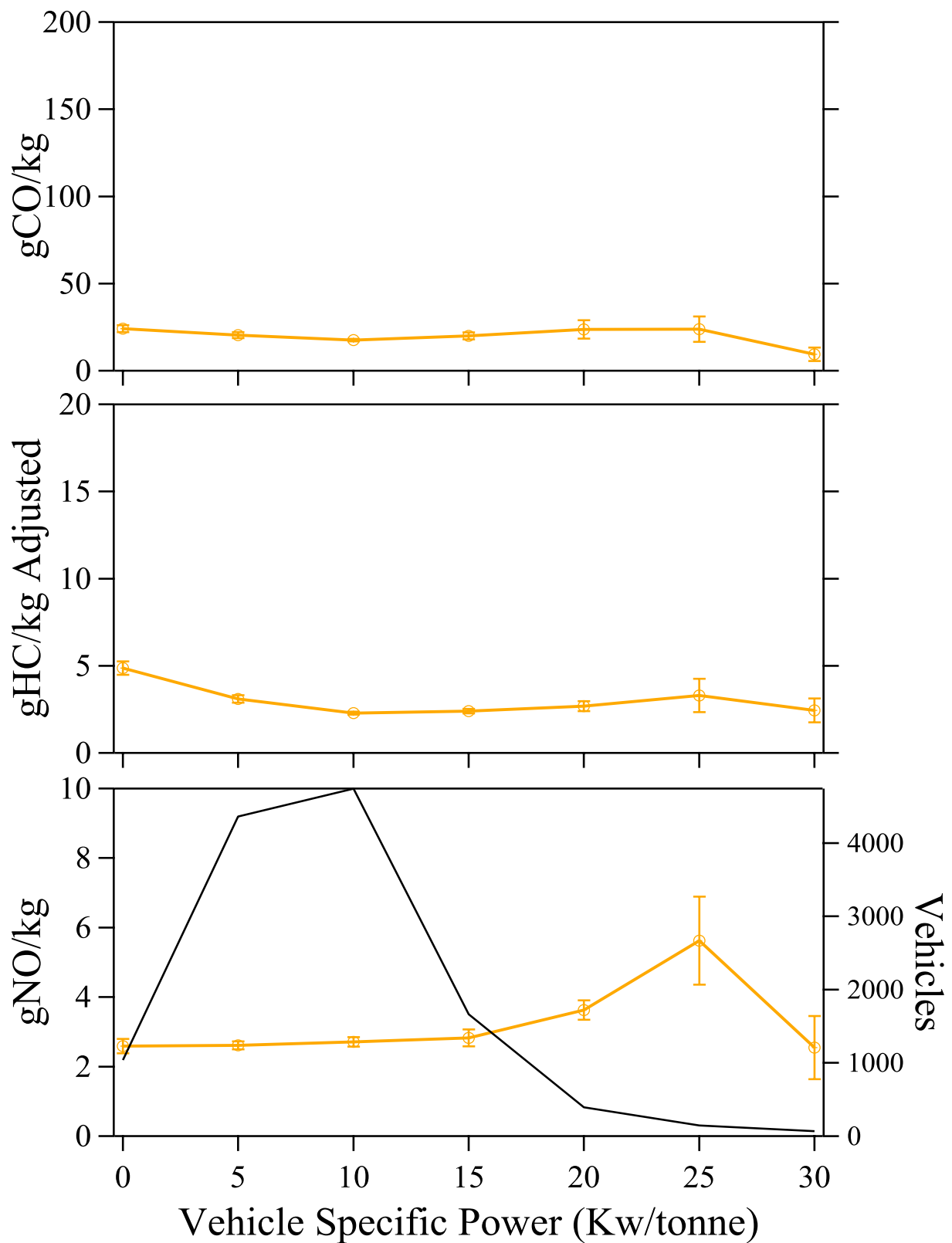
Figure 17. Vehicle emissions as a function of vehicle specific power for the Fresno data with valid speed and acceleration measurements. Error bars are standard errors of the mean calculated from daily samples and the solid line in the bottom graph is the number of vehicles in each bin.
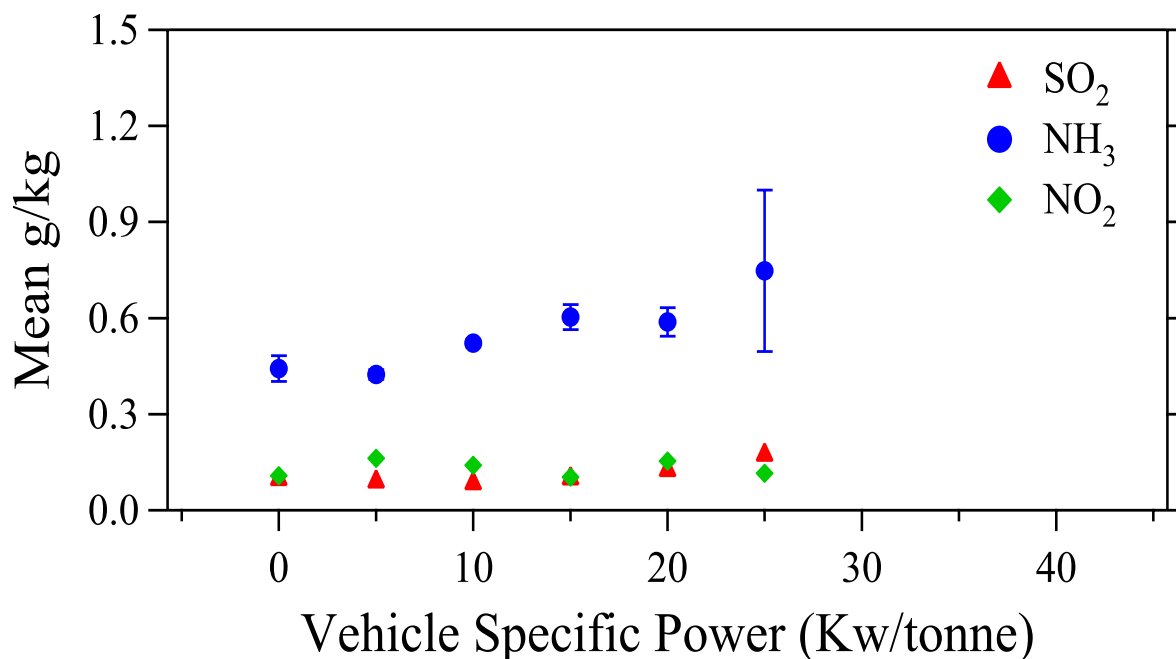
Figure 18. SO_2, NH_3 and NO_2 emissions as a function of vehicle specific power for the 2008 Fresno data with valid speed and acceleration measurements. The NH_3 error bars are standard errors of the mean calculated from daily samples.

RESULTS FOR WEST LOS ANGELES

Measurements were made on five consecutive weekdays, from Monday, March 17, to Friday, March 21, between the hours of 7:30 and 19:00 on the uphill ramp. This intersection is just west of the location where La Brea Ave. passes under I-10. The instrument was located as far up the ramp as possible, this same location as was used during the IMRC measurements in 1999 and for all of the Coordination Research Council sponsored measurements in 2001, 2003 and 2005. A satellite photo of the measurement location is shown in Figure 19 and a photograph of the ramp is shown in Figure 20. The uphill grade at the measurement location is 2°. Appendix C gives temperature and humidity data for the 1999, 2001, 2003, 2005 and 2008 studies from Los Angeles International Airport, approximately eight miles southwest of the measurement site. Following the five days of data collection the images were read for license plate identification. Plates that appeared to be in state and readable were sent to the State of California to have the vehicle make and model year determined. The resulting database contained 17,953 records with make and model year information and valid measurements for at least CO and CO_2. Most of these records also contain valid measurements for HC, NO, SO_2, NH_3 and NO_2 as well. This and all previous databases can be found at www.feat.biochem.du.edu.

The validity of the attempted measurements is summarized in Table 7. The table describes the data reduction process beginning with the number of attempted measurements and ending with the number of records containing both valid emissions measurements and vehicle registration information. A complete description of the process has been provided in the San Jose results section and the measurement error rejection criteria are provided in Appendix A.

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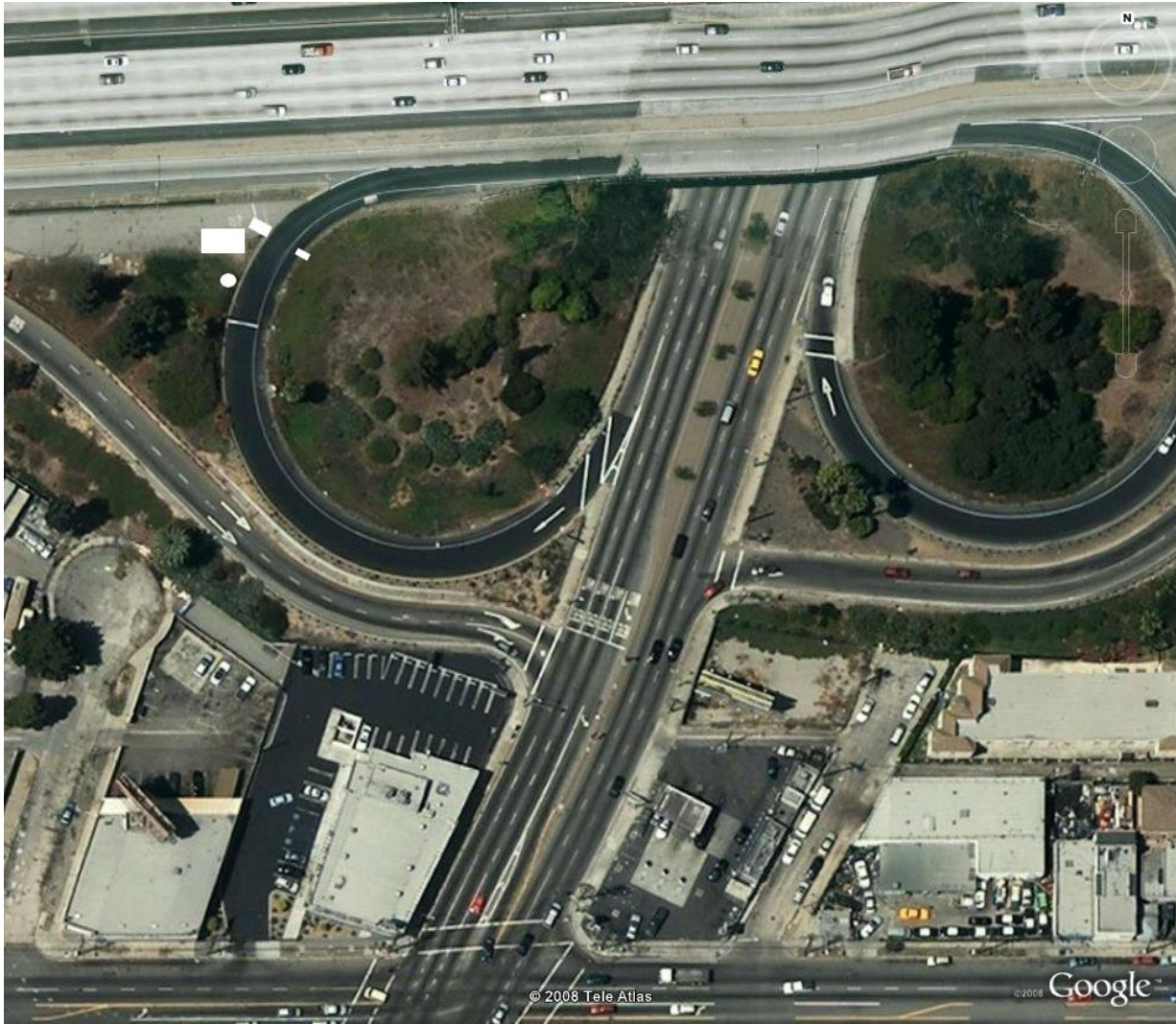
Figure 19. A satellite view of the West LA on-ramp from southbound La Brea Blvd. to eastbound I-10 with the approximate locations of the motor home (large rectangle), the remote sensing detector, source (small rectangles) and camera (circle).

Table 8 provides an analysis of the number of vehicles that were measured repeatedly, and the number of times they were measured. Of the 17,953 records used in this fleet analysis, 11,285(62.8%) were contributed by vehicles measured once, and the remaining 6,668 (37.2%) records were from vehicles measured at least twice.

Table 9 is the historic data summary; included are summaries of previous remote sensing databases collected by the University of Denver at the West Los Angeles site. The other measurements were conducted in November of 1999, October 2001, 2003 and 2005. The average HC values have been adjusted to remove an artificial offset in the measurements as previously discussed. Most notable change from the previous measurements is an increase in the average NO emissions.

Figure 20. The West LA monitoring site with the measurement beam located at the end of the guardrail, to the right of the motor home. The vehicle stopped at the light is 84ft. from the measurement location.

Table 7. West Los Angeles Validity Summary.

	CO	HC	NO	SO$_2$	NH$_3$	NO$_2$
Attempted Measurements	23,579					
Valid Measurements	22,072	22,072	21,997	22,051	22,067	21,963
Percent of Attempts	93.6%	93.6%	93.3%	93.5%	93.6%	93.1%
Submitted Plates	18,323	18,286	18,308	18,318	18,230	18,249
Percent of Attempts	77.7%	77.6%	77.6%	77.7%	77.3%	77.4%
Percent of Valid Measurements	83.0%	82.8%	83.2%	83.1%	82.6%	83.1%
Matched Plates	17,953	17,916	17,939	17,948	17,860	17,880
Percent of Attempts	76.1%	76.0%	76.1%	76.1%	75.7%	75.8%
Percent of Valid Measurements	81.3%	81.1%	81.6%	81.4%	80.9%	81.4%
Percent of Submitted Plates	98.0%	98.0%	98.0%	98.0%	98.0%	98.0%

Table 8. West Los Angeles number of measurements of repeat vehicles.

Number of Times	Number of Vehicles	Percent of Measurements
1	11,258	62.8%
2	1,473	16.4%
3	635	10.6%
4	378	8.4%
5	55	1.5%
6	4	0.1%
7	2	0.1%
>7	1	0.1%

Mean fleet emissions have decreased at the LA site as at the San Jose site between 1999 and 2008 with reductions of 70%, 74% and 43% for CO, HC and NO respectively. The mean model year in West Los Angeles has kept pace with the measurement schedule. The percentage of emissions from the dirtiest 10% of the measurements increased for all pollutants.

The inverse relationship between vehicle emissions and model year is shown in Figure 21, for data collected during each of the five years. The HC data have been offset adjusted here for comparison. The 2008 CO and HC emissions follow a similar pattern of the previous data sets while the 2008 NO emissions increase along a much steeper slope. The only major difference between the 2008 data and the previous data sets is the time of year that the data was collected. However, the observed temperature and humilities (see Appendix C) is consistent with those experienced in previous year. Since this is a traffic light controlled on-ramp, changes in the driving mode observed should be small and the measured speed and accelerations seem to confirm this.

Figure 22 is the same plot for SO_2, NH_3 and NO_2 that were collected for the first time with the 2008 measurements. SO_2 and NH_3 show a model year dependence, increasing with age, while NO_2 shows no model year dependence. The NH_3 emissions are highest at this site owing in part to the driving mode and the larger NO emissions that are a necessary step for NH_3 production.

Figures 23 – 25 are plots of the west Los Angeles vehicle emissions by model year, with each model year divided into emission quintiles. The bars represent the mean emissions for each quintile, and do not account for the number of vehicles in each model year. As seen in these plots at the west Los Angeles site the cleanest 60% of the vehicles, regardless of model year, make a negligible contribution to the total fleet emissions. In addition the Tier 1 cut-points of 34, 2.5 and 4.9 gm/kg of CO, HC and NO show that significant fractions of vehicles in Fresno are measured below these levels.[20] Comparing the fleet fractions versus model year plots with the previous two sites shows that the new car sales at the west Los Angles site was recession proof. The increases in fleet fractions are unbroken until the 2007 model year.

Figure 26 uses equation (4) to calculate the vehicle specific power in kW/metric tonne was calculated for all measurements in each of the four years' databases. All of the specific power bins contain at least 100 measurements except for the VSP bin of 30 in 1999, 2001 and 2005 which contain 77, 69 and 90 measurements, respectively. The HC data have been offset adjusted

Table 9. West Los Angeles Site Historic Data Summary.

Study Year	1999	2001	2003	2005	2008
Mean CO (%) (g/kg of fuel)	0.58 (70.3)	0.44 (56.2)	0.34 (42.4)	0.22 (27.3)	0.17 (21.4)
Median CO (%)	0.09	0.06	0.06	0.03	0.02
Percent of Total CO from Dirtiest 10% of the Fleet	67.4%	72.4%	72.2%	77.0%	80.7%
Mean HC (ppm)* (g/kg of fuel)* Offset (ppm)	195 (7.0) -60	125 (4.6) -21	121 (4.5) -35	84 (3.2) 65/0†	50 (1.8) 10
Median HC (ppm)*	70	39	45	40	10
Percent of Total HC from Dirtiest 10% of the Fleet	57%	61.6%	60.3%	78.0%	81%
Mean NO (ppm) (g/kg of fuel)	477 (6.6)	411 (5.6)	323 (4.5)	242 (3.4)	265 (3.75)
Median NO (ppm)	116	72	48	24	11
Percent of Total NO from Dirtiest 10% of the Fleet	51.6%	54.9%	59.3%	66.9%	71%
Mean SO_2 (ppm) (g/kg of fuel)	NA	NA	NA	NA	2 (0.07)
Median SO_2 (ppm)	NA	NA	NA	NA	0.2
Percent of Total SO_2 from Dirtiest 10% of the Fleet	NA	NA	NA	NA	100%
Mean NH_3 (ppm) (g/kg of fuel)	NA	NA	NA	NA	99 (0.8)
Median NH_3 (ppm)	NA	NA	NA	NA	34
Percent of Total NH_3 from Dirtiest 10% of the Fleet	NA	NA	NA	NA	50.8%
Mean NO_2 (ppm) (g/kg of fuel)	NA	NA	NA	NA	4 (0.08)
Median NO_2 (ppm)	NA	NA	NA	NA	2
Percent of Total NO_2 from Dirtiest 10% of the Fleet	NA	NA	NA	NA	61.8%
Mean Model Year	1992.4	1994.4	1996.5	1998.9	2001.2
Mean Speed (mph)	17.6	18.3	17.0	17.7	17.6
Mean Acceleration (mph/s)	1.4	1.4	1.9	1.7	1.9
Mean VSP (kw/tonne) Slope (degrees)	9.0 2.0°	10.3 2.0°	11.6 2.0°	11.4 2.0°	12.2 2.0°

*Indicates values that have been HC offset adjusted as described in text.
†Only the October 17th data was offset adjusted, the remaining days had a zero offset.
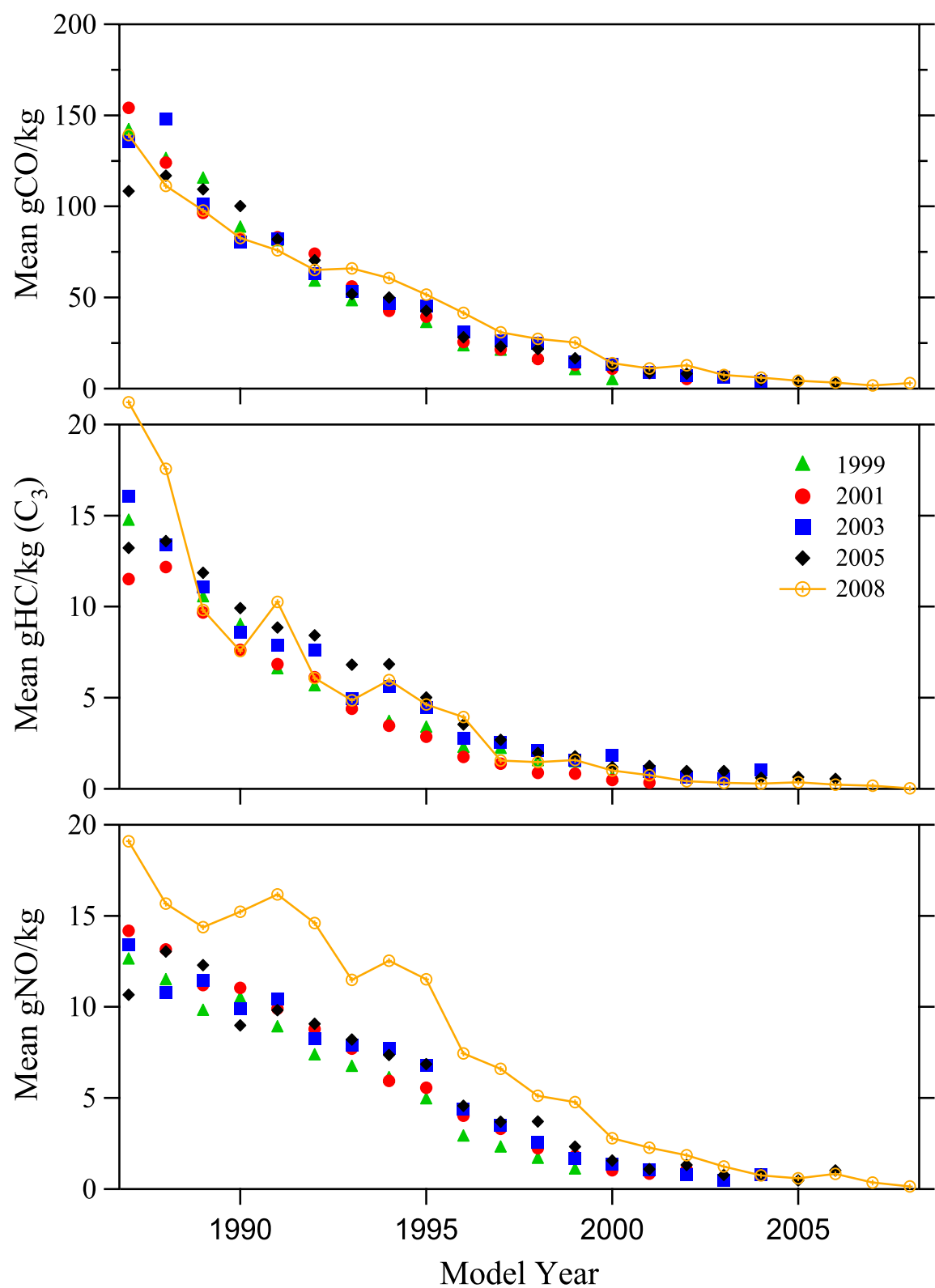
**Figure 21.** Mean vehicle emissions illustrated as a function of model year. HC data have been offset adjusted as described in the text.
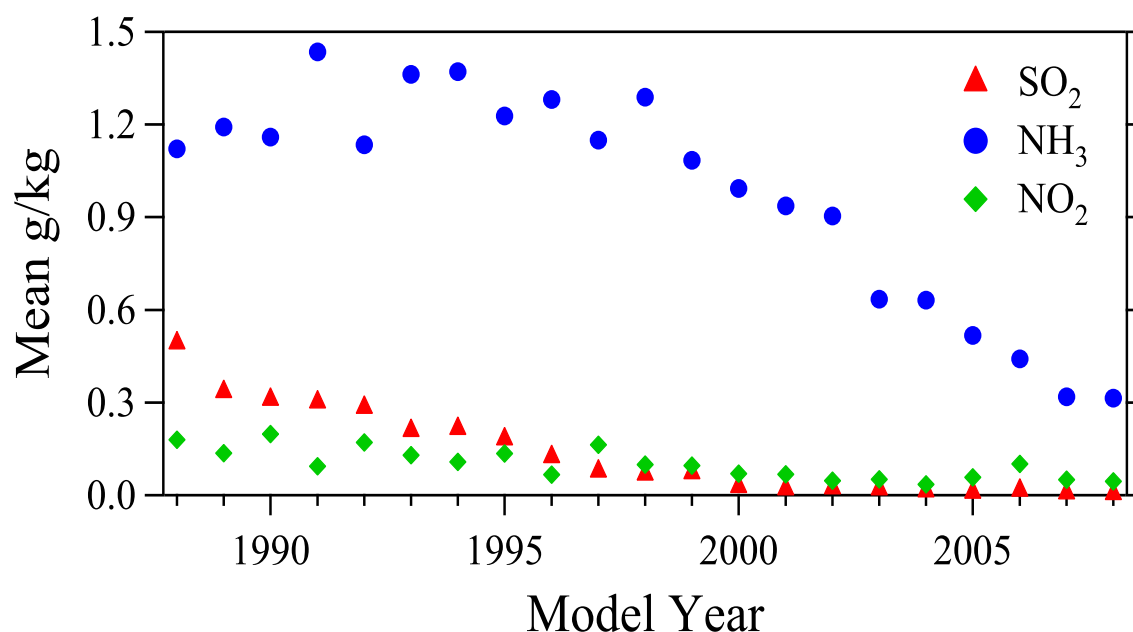
**Figure 22.** SO_2, NH_3 and NO_2 mean vehicle emissions of as a function of model year for the 2008 West Los Angeles measurements.

for this comparison. The error bars included in the plot are standard errors of the mean calculated from the daily averages.

In general all of the emissions continue to decrease with each set of data. The HC emissions continue to show a negative dependence on specific power while the CO and NO plots continue to show less and less dependence on VSP at this site. In spite of the fact that this is a traffic light controlled on ramp that encourages aggressive drivers both CO and NO emissions appear to be better controlled each year. However, the 2008 data set shows significant increases in NO emissions at the lower VSP bins as reflected in the increased average. The error bars included in the plot are standard errors of the mean calculated from the daily averages. These uncertainties were generated for these γ-distributed data sets by applying the central limit theorem. Each day's average emissions for a given VSP bin were assumed an independent measurement of the emissions at that VSP. Normal statistics were then applied to these daily averages.

Figure 27 is the plot of the emissions of SO_2, NH_3 and NO_2 as a function of vehicle specific power for the 2008 measurements. The NH_3 error bars included in the plot are standard errors of the mean calculated from the daily averages. NH_3 is the only species to show any dependence on driving mode with a positive dependence.

Using VSP, it is possible to reduce the influence of driving behavior in the mean vehicle emissions. Table 10 shows the mean emissions from all vehicles in the 1999, 2001, 2003, 2005 and 2008 databases with vehicle specific powers between −5 and 20 kw/tonne (this range has been picked because it coincides with the VSP range observed on the Federal Test Procedure). Note that these emissions do not vary considerably from the mean emissions for the entire

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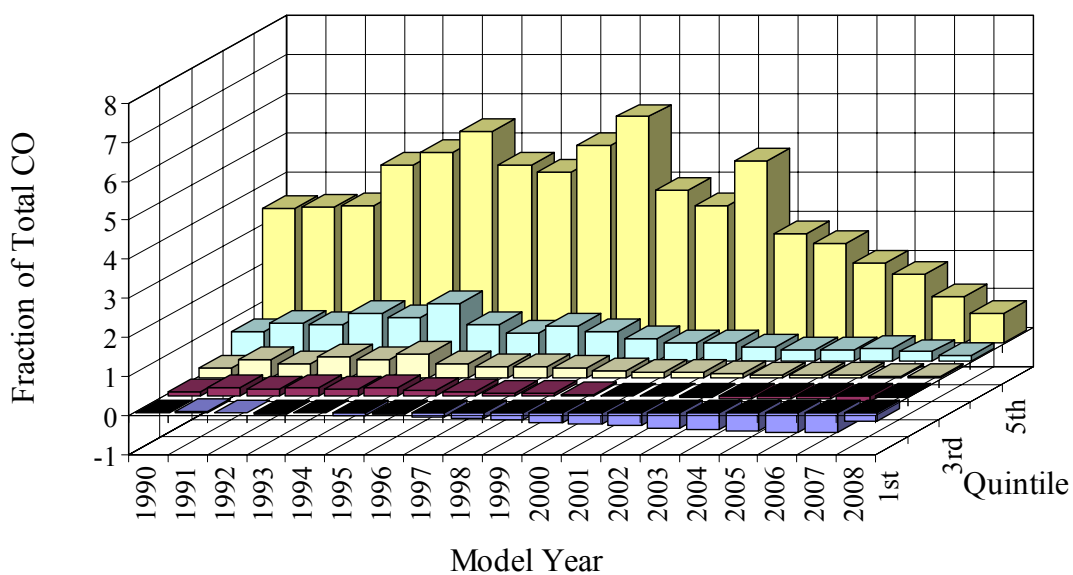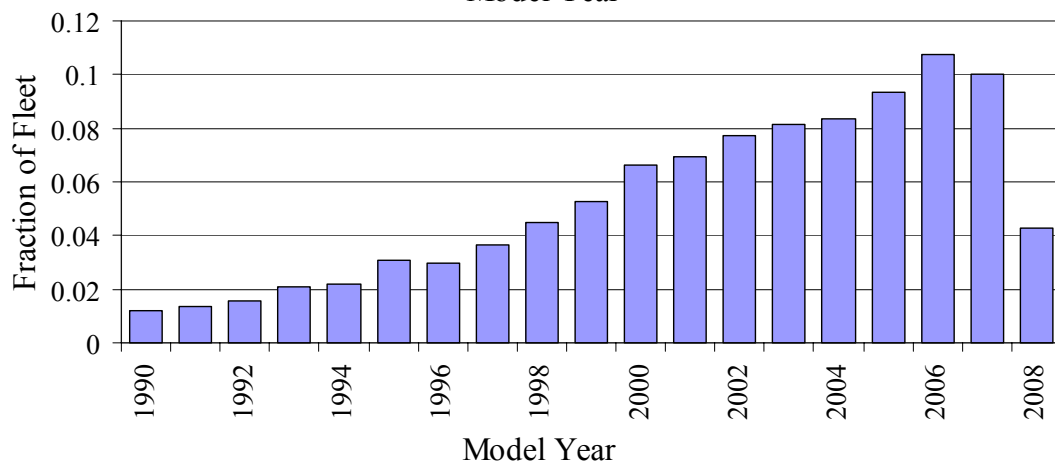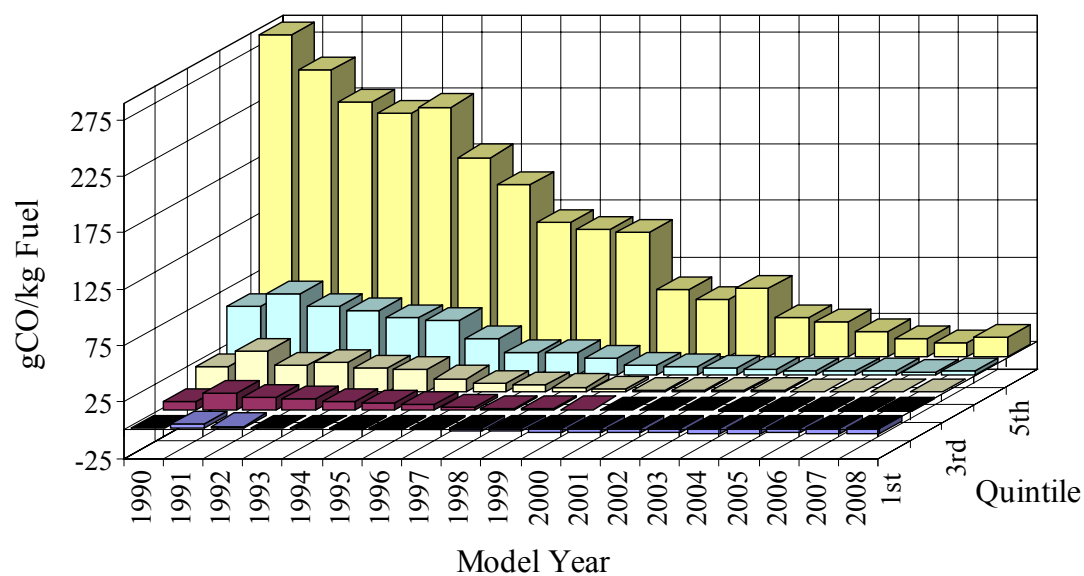
Figure 23. 2008 West LA CO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional CO emissions by model year and quintile (bottom).
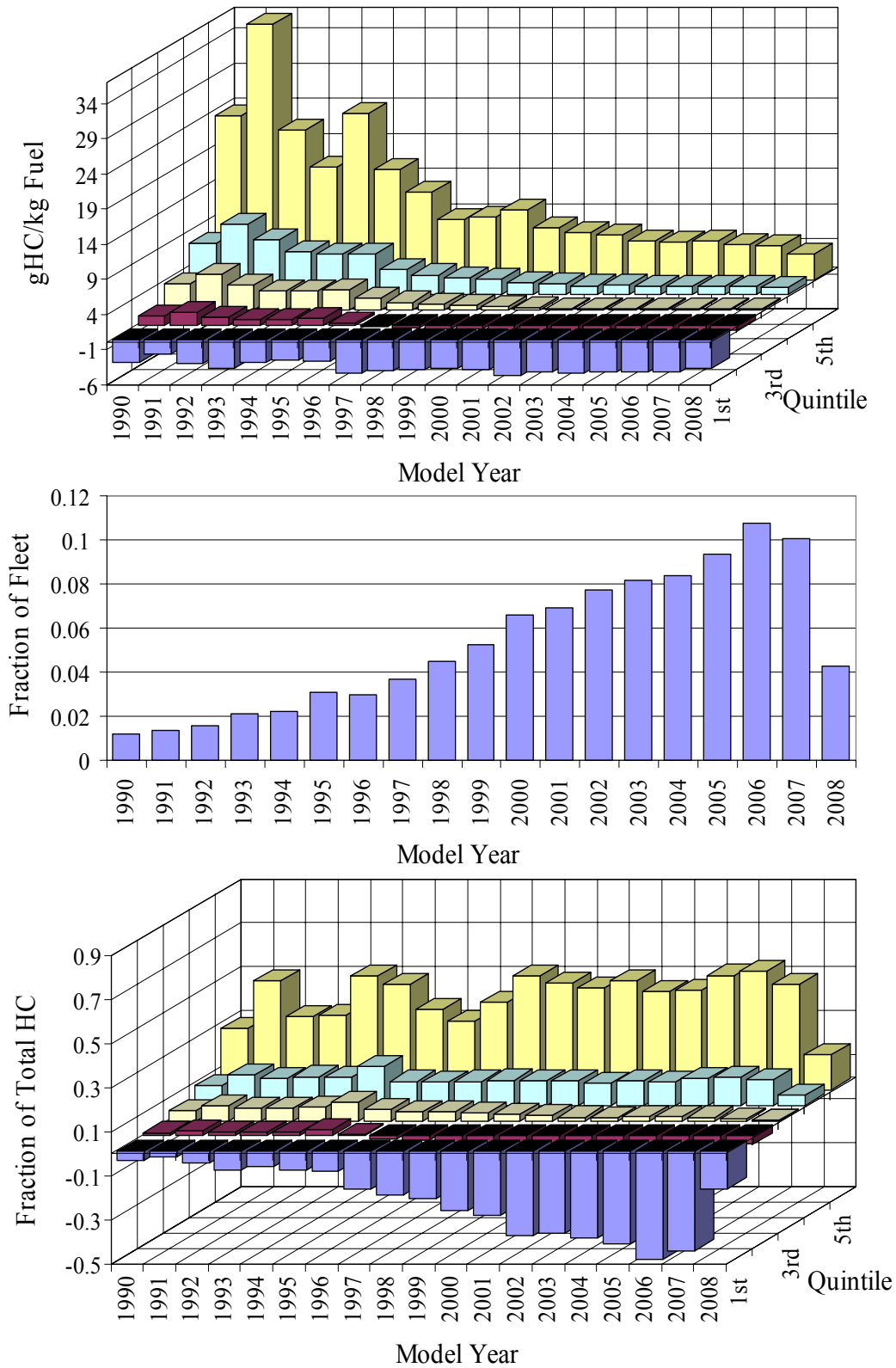
Figure 24. 2008 West LA HC emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional HC emissions by model year and quintile (bottom).
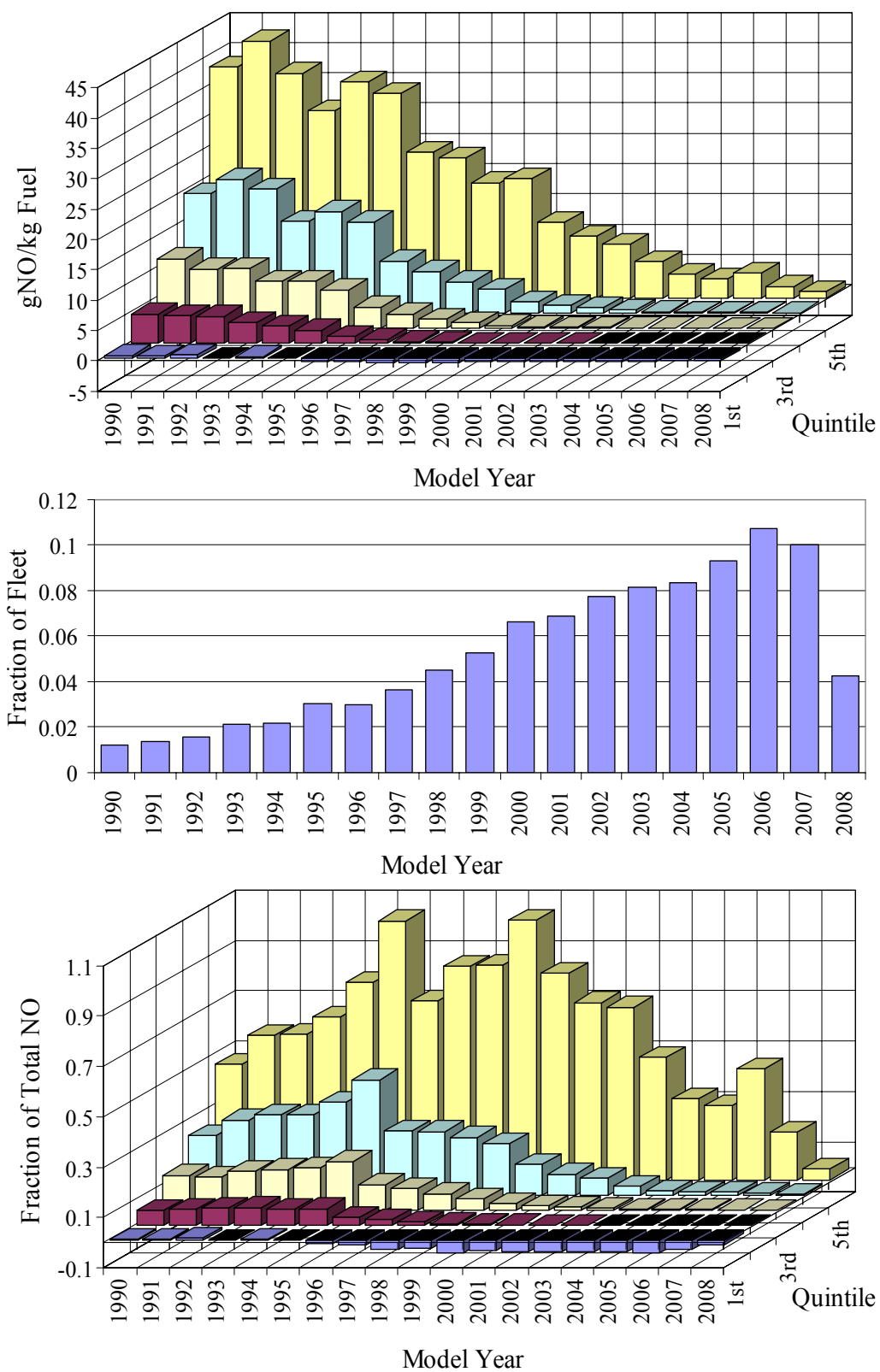
Figure 25. 2008 West LA NO emissions by model year and quintile (top), fleet distribution (middle) and their product showing the total fractional NO emissions by model year and quintile (bottom).
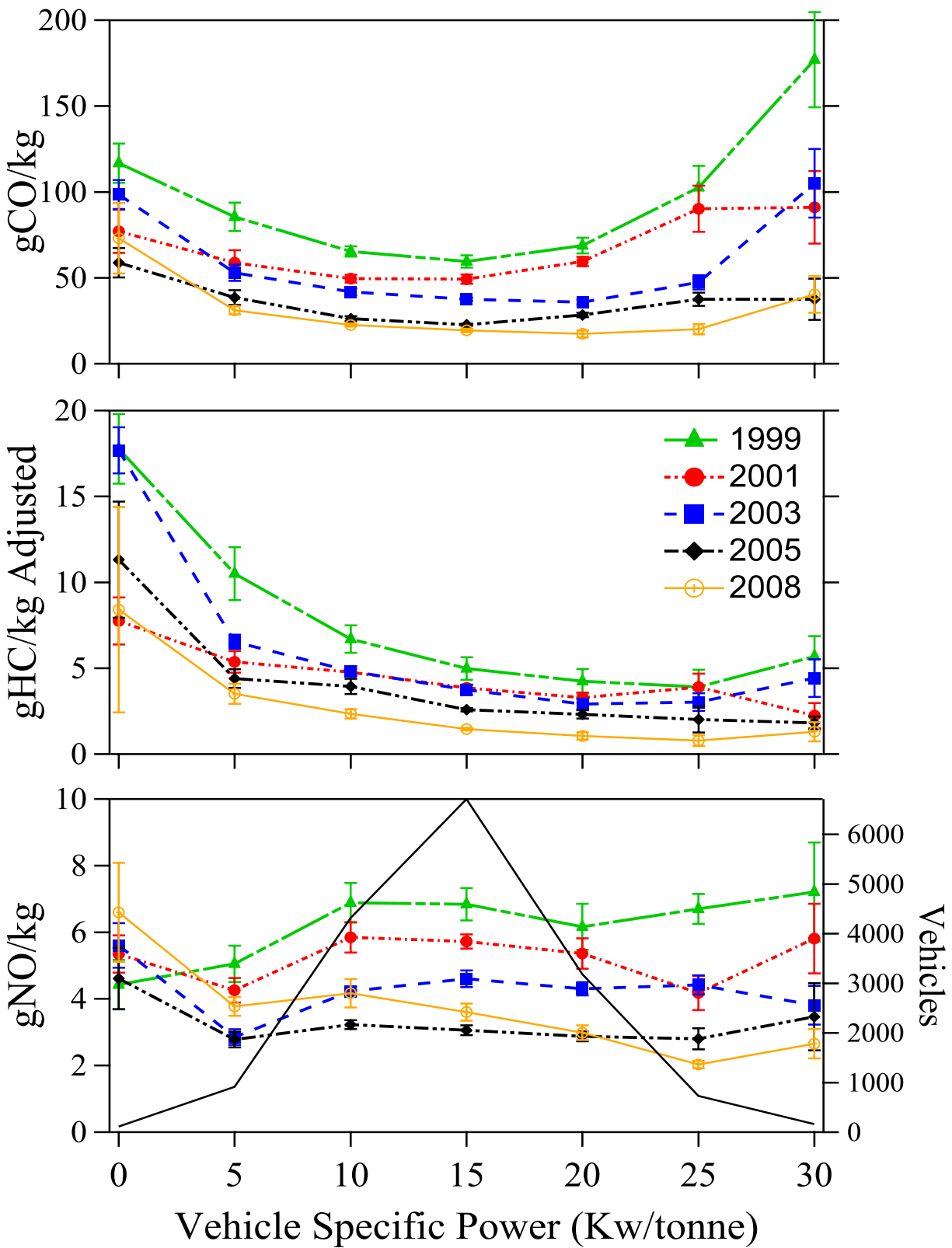
**Figure 26.** Vehicle emissions as a function of vehicle specific power for all of the West LA data sets. Error bars are standard errors of the mean calculated from daily samples and the solid line in the bottom graph is the number of vehicles in each bin for the 2008 data.
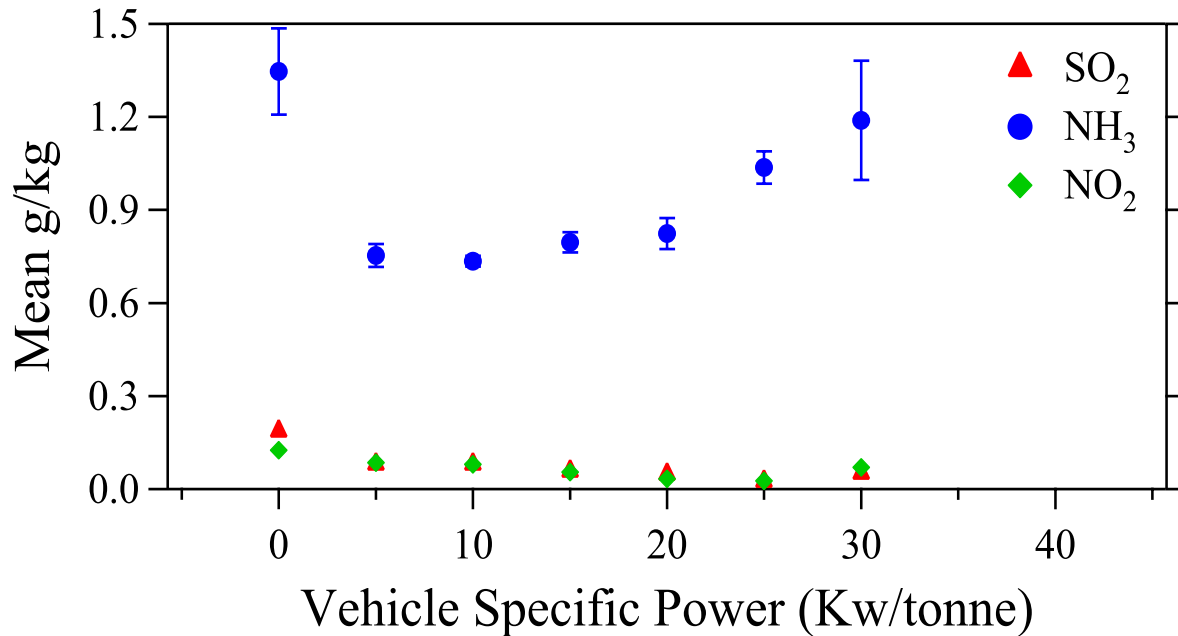
Figure 27. SO_2, NH_3 and NO_2 emissions as a function of vehicle specific power for the 2008 West Los Angeles data with valid speed and acceleration measurements. The NH_3 error bars are standard errors of the mean calculated from daily samples.

databases, as shown in Table 9. Also shown in Table 10 are the mean emissions for the 1999, 2001, 2003, 2005 and 2008 databases, adjusted for vehicle specific power to match the 1999 VSP distribution. This correction is accomplished by applying the mean vehicle emissions for each VSP bin (between –5 and 20 kw/tonne) from a certain year's measurements to the vehicle distribution, by vehicle specific power, for each bin from 1999. A sample calculation, for the vehicle specific power adjusted mean NO emissions, is shown in Appendix D. The HC emissions in 2003 show increased emissions at the low VSP levels (see Figure 26) raising the adjusted emissions.

Table 10. Vehicle specific power adjusted fleet emissions (-5 to 20 kw/tonne only) with standard error of the means calculated using daily averages.

Species	1999 measured (adjusted)	2001 measured (adjusted)	2003 measured (adjusted)	2005 measured (adjusted)	2008 measured (adjusted)
Mean gCO/kg	68.1 ± 2.1 (68.1 ± 2.1)	52.5 ± 2.5 (52.9 ± 2.6)	40.3 ± 1.0 (43.7 ± 1.0)	26.1 ± 0.6 (28.0 ± 0.7)	21.1 ± 0.5 (23.8 ± 0.6)
Mean gHC/kg[a]	9.1 ± 0.7 (6.7 ± 0.7)	5.2 ± 0.2 (4.5 ± 0.2)	5.7 ± 0.3 (4.9 ± 0.3)	2.8 ± 0.7 (3.5 ± 0.1)	1.8 ± 0.1 (2.2 ± 0.1)
Mean gNO/kg	6.4 ± 0.5 (6.4 ± 0.5)	5.6 ± 0.3 (5.5 ± 0.3)	4.3 ± 0.2 (4.2 ± 0.2)	3.1 ± 0.1 (3.1 ± 0.1)	3.7 ± 0.3 (3.8 ± 0.3)

[a]HC emissions are offset adjusted for all of the years' adjusted data.

Because all VSP data are adjusted to the 1999 vehicle distribution by VSP bin, the 1999 adjusted values are the same as the measured values except for the HC data that includes an extra calculation to adjust for the yearly HC offset.

A similar normalization can be applied to a fleet of specific model year vehicles to track deterioration, provided we use as a baseline only the model years measured in 1999. A sample calculation, for the model year adjusted mean NO emissions, is shown in Appendix E. Table 11 shows the mean emissions for all vehicles from model year 1984 to 2000, as measured in each of the four years. Applying the vehicle frequency distribution by model year from 1999 to the mean emissions by model year from the later studies yields the model year adjusted fleet emissions. The calculation indicates that, although some of the measured decrease in fleet average emissions is due to fleet turnover, the emissions of even the older model years (1984-2000) measured previously has not increased significantly. The lack of emissions deterioration over a growing period of time is likely due to many cumulative factors that are dominated by improvements in emission controls function and durability.[19] Note that the fleet of 1984 – 2000 model year vehicles has shrunk about 64% from 1999 and the values presented here include not only vehicle emission deterioration, but all the mechanisms which result in vehicles being permanently removed from the fleet. The slowly increasing emissions suggest that vehicle retirement is positively correlated with higher emissions.

Table 11. Model year adjusted fleet emissions (MY 1984-2000 only). Errors are standard error of the means calculated from the daily means.

Species	1999 measured (adjusted)	2001 measured (adjusted)	2003 measured (adjusted)	2005 measured (adjusted)	2008 measured (adjusted)
Mean gCO/kg	60.6 ± 2.0 (60.6 ± 2.0)	52.1 ± 2.3 (61.1 ± 2.7)	51.5 ± 1.6 (65.6 ± 2.0)	43.0 ± 0.7 (61.4 ± 0.9)	46.2 ± 0.9 (68.1 ± 1.3)
Mean gHC/kg[a]	8.3 ± 0.6 (5.9 ± 0.6)	5.2 ± 0.2 (5.2 ± 0.2)	6.8 ± 0.3 (6.7 ± 0.3)	4.5 ± 0.6 (6.9 ± 0.2)	4.6 ± 0.3 (3.4 ± 0.2)
Mean gNO/kg	6.2 ± 0.4 (6.2 ± 0.4)	6.1 ± 0.4 (7.0 ± 0.4)	5.8 ± 0.2 (7.0 ± 0.3)	5.5 ± 0.2 (7.3 ± 0.3)	8.3 ± 0.6 (11 ± 0.8)
Vehicles[b]	17,903/17,798	17,304/17,194	13,827/13,786	10,125/10,111	6,498/6,481

[a]HC emissions are offset adjusted for all of the years adjusted data.
[b]Number of vehicles in the CO mean / number of vehicles in the HC and NO means.

Vehicle emissions deterioration is also illustrated in Figure 28, which shows the mean emissions of the 1984 to 2006 model year fleet as a function of vehicle age. The first point for most model years was measured in 1999, the second point in 2001, etc. The HC emissions have been offset adjusted for comparison. Vehicle age was defined as the difference between the year of measurement and the vehicle model year. Three features of this analysis stand out. The first is the fact that new vehicle certification emissions regulations overall have been very successful. The second is the gap between the 1996 and newer model year vehicles and the older fleets.
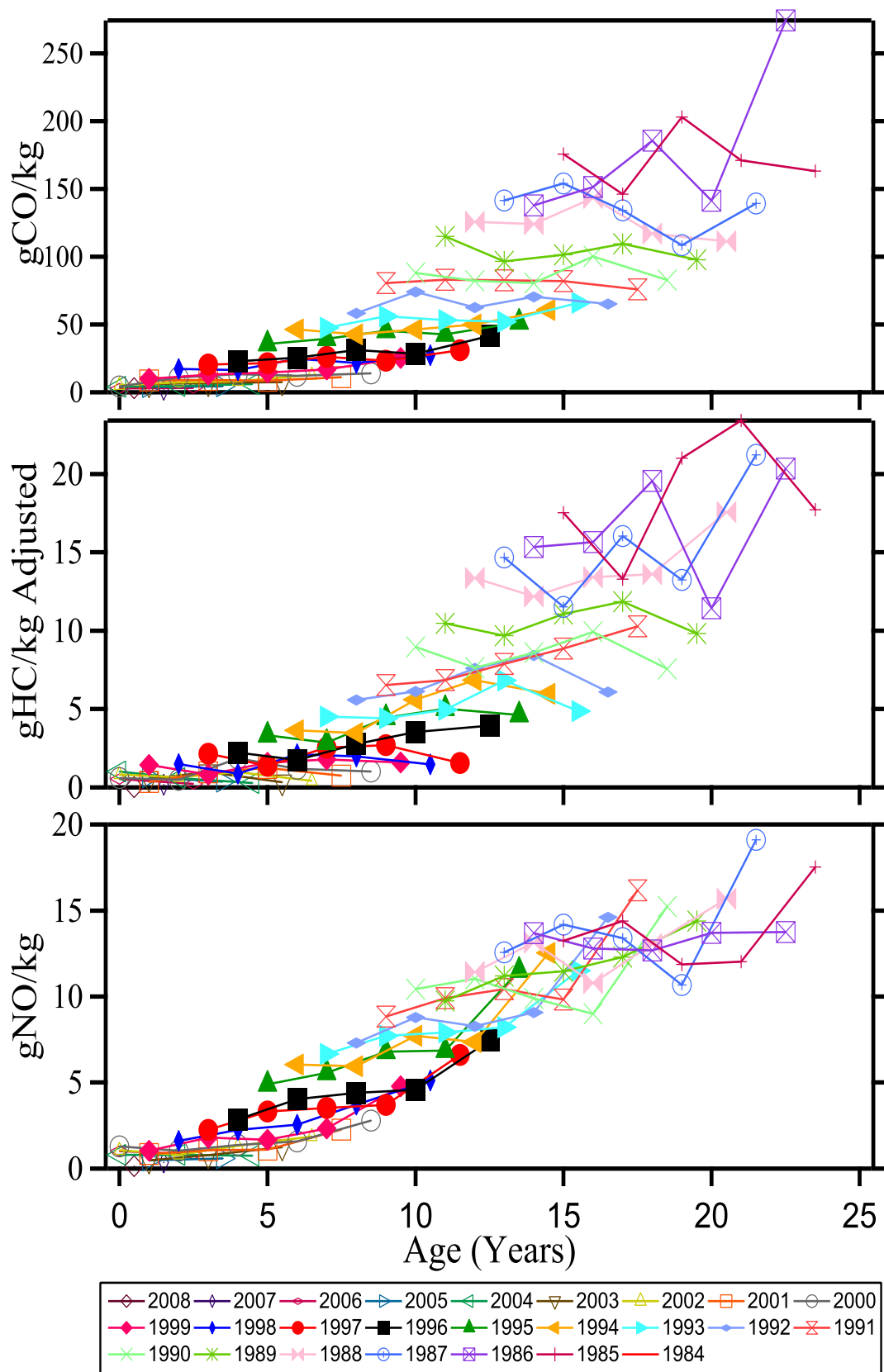
Figure 28. Mean vehicle emissions as a function of age, shown by model year.

There were significant changes in the motor vehicle emissions regulations for the 1996 model year, most notably the introduction of two additional oxygen sensors to monitor catalyst efficiency as part of the OBDII monitoring system. That 1996 (OBDII) model year vehicles entered the fleet with lower emissions is purely a function of technology. The fact that they continue more than a decade later to remain significantly lower emitting than 1995 model year and older can be a function of the driver's response to the OBDII system, or a function of the technology itself. We can not unequivocally distinguish between the two. We have anecdotal information confirmed by patent literature that these additional oxygen sensors allow the manufacturers to correct for any drift that occurs with the manifold oxygen sensor that is used to maintain the engines air to fuel setting.[23]

The third feature, common to the E-23 data, is that each model year shows little deterioration with age, but each older model year has higher emissions than its newer neighbor. The various analyses of the data presented up to this point suggest small increases in emissions from the previous years even, when model year adjustments were made to remove effects of fleet turnover. The lack of larger deterioration rates also shows up clearly in Figure 28. We can imagine several programs and processes that may contribute to the overall fleet emissions: improvements in California's I/M program, the use of reformulated gasoline,[24] decreases in deterioration rates as a result of the implementation of OBDII diagnostic systems and the "natural" loss of the least well maintained vehicles as fleets age. The enhanced Smog Check II I/M program was phased in during 1998.[11] The fact that the same phenomenon is seen in the newest model years that are not subject to I/M until their fifth model year indicates that I/M effectiveness cannot be the whole story. It is also difficult to construct a story whereby fuel changes could somehow stop vehicle emissions deterioration. Figure 29 is a plot of emissions deterioration rates calculated from the data in Figure 28. We have assumed that vehicle emissions deterioration can be modeled as a linear process and have fitted lines to each model year's emissions data. The resulting slope of that line is an emissions deteriorations rate in grams of emissions per kilogram of fuel used per year.

If the OBDII check engine light increases or improves emission related repairs for vehicles we should expect that to result in a decrease in emission deterioration rates, especially between the transition model years of 1995 and 1996. Figure 29 shows that there is no significant statistical difference in the emissions deterioration rates between the 1995 and 1996 model years, even though there is a statistical difference in emission levels. Figure 29 does give some support to the idea that poorer maintained vehicles have shorter lifetimes as both the CO and NO emission deterioration rates show decreases for 1992 model year fleets and older.

Instrument noise was measured using the slope of the negative portion of a plot of the natural log of the binned emission measurement frequency versus the emission level. Such plots were constructed for the three primary pollutants. Linear regression gave best fit lines whose slopes correspond to the inverse of the Laplace factor, which describes the noise present in the measurements. This factor must be viewed in relation to the average measurement for the particular pollutant to obtain a description of noise. The Laplace factors were 3.0, 2.8, 0.4, 0.04, 0.01 and 0.2 for CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These values indicate standard
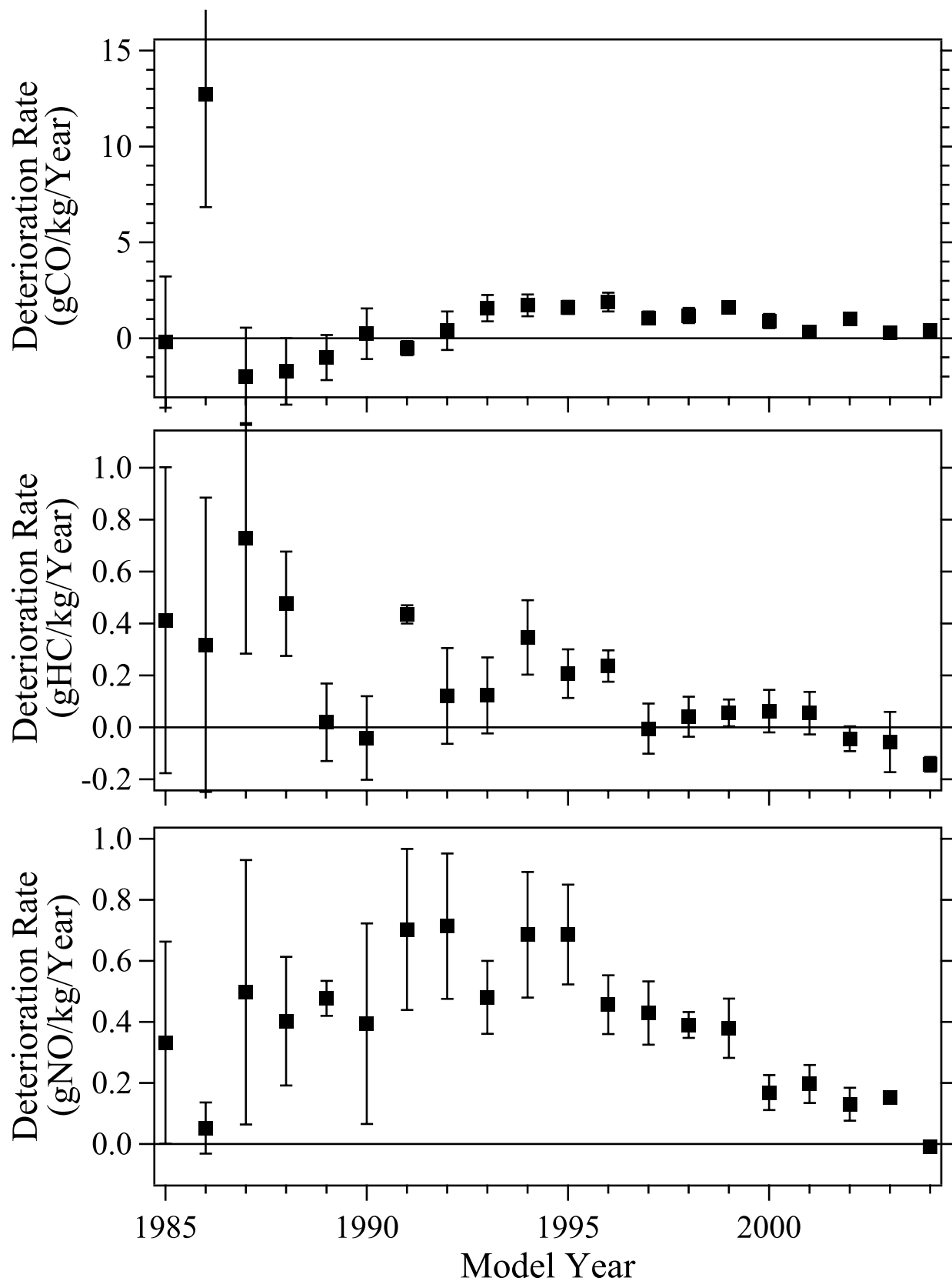
Figure 29. On-road emissions deterioration rates vs. model year for the West LA sampling location. The uncertainty bars plotted are the standard error of the slope for the least-squares fit.

deviations of 4.2 g/kg (0.03%), 4.0 g/kg (94ppm), 0.5 g/kg (37ppm), 0.05 g/kg (2ppm), 0.02 g/kg (3ppm) and 0.2 g/kg (11ppm) for individual measurements of CO, HC, NO, SO_2, NH_3 and NO_2, respectively. These levels are consistent with the low noise level as discussed in a previous Phoenix report.[22] In terms of uncertainty in average values reported here, the numbers are reduced by a factor of the square root of the number of measurements. For example, with averages of 100 measurements, which is the low limit for number of measurements per bin, the uncertainty reduces by a factor of 10. Thus, the uncertainties in the averages of 100 measurements reduce to 0.4 g/kg, 0.4 g/kg, 0.05 g/kg, 0.005 g/kg, 0.002 g/kg and 0.02 g/kg respectively. Note that these noise factors average to zero and do not alter the reported mean values.

DISCUSSION

Most emission species emitted by light-duty vehicles have skewed distributions where a small percentage of the measurements account for a large percentage of the total emissions. Table 9 details the West LA historical data showing how as vehicle emissions have decreased over time the fraction of emissions produced by dirtiest 10% of the measurements have increased significantly. For the San Jose measurements Table 3 includes data for HC that contradicts the historical observations from the West LA site.

When making historical comparisons it helps when the sampling location and driving mode remain similar for the two measurement periods. We are uncertain of the exact measurement location used for the 1999 San Jose measurements, but photographs of those measurements have allowed us to get reasonably close. Driving mode is harder to control as increases or decreases in congestion, construction issues or changes in the highway layout up or down stream can affect the driving mode. HC emissions are especially sensitive to driving modes that can result in rapid engine decelerations, such as when one simply takes their foot off of the accelerator pedal. These types of events increase g/kg emissions and are difficult for our speed and acceleration measurement system to detect because the decelerations are not as rapidly transmitted to the body of the vehicle as they are to the engines and the resulting emissions.

Figure 30 is a comparison of the two gHC/kg emissions distributions for the San Jose and West La sites. The West LA site is a traffic light controlled on-ramp that favors low speed accelerations with little congestion while the traffic at the San Jose site is at both higher speeds and more congestion. What the comparison shows is that the fleet fractions at the San Jose site are shifted to higher gHC/kg bins. The negative tail at San Jose has fewer measurements (11.6% versus 17.4%) than the West LA site. These San Jose measurements show up in the positive bins between 0 and 10. This shift changes the weighting seen at the San Jose site and reduces the skewness of the overall emissions distribution and significantly reduces the fraction of emissions that the last decile of measurements accounts for.

The production of NH_3 emissions is contingent upon the vehicles ability to produce NO in the presence of a catalytic convertor that has enough stored hydrogen to reduce that NO to NH_3. Without either of these species the formation of exhaust NH_3 is precluded. Dynamometer studies have shown that these conditions are met when acceleration events are preceded by a deceleration event though not necessarily back to back.[25] The calculated average NH_3 emissions
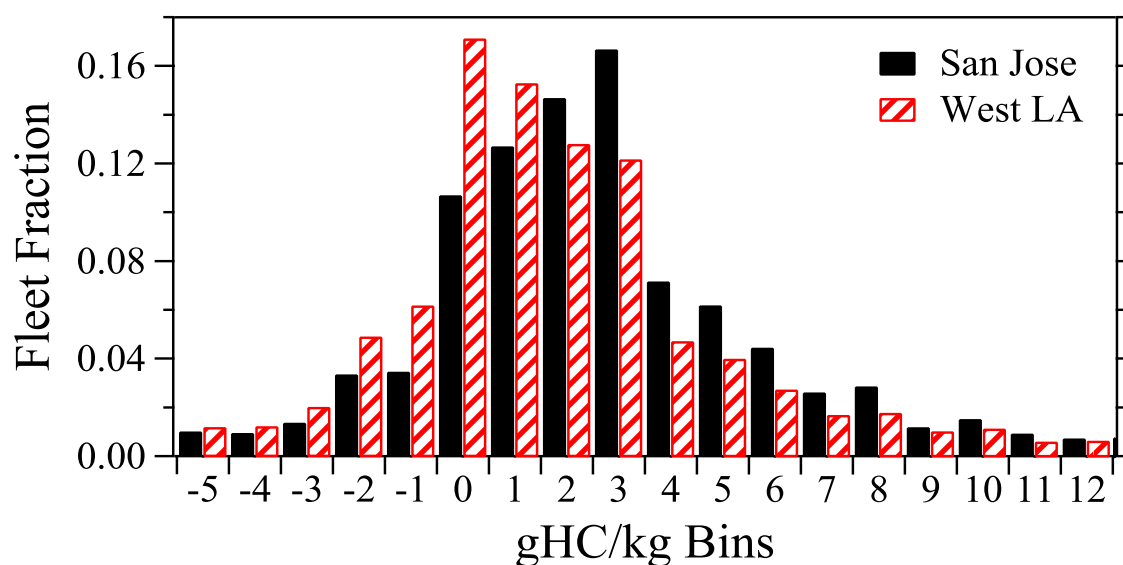
Figure 30. Comparison of the fleet fractions found for binned gHC/kg emission measurements between the San Jose and West LA sites.

for the California fleet is 0.58 ± 0.04. The average however is misleading as there are two different measurement magnitudes among the three sites. Figure 31 is a composite gNH$_3$/kg emissions as a function of model year for the three measurement sites. As the figure shows San Jose and Fresno have similar fleet NH$_3$ emissions profiles with means of 0.48 ± 0.01 and 0.49 ± 0.01 while the data collected at the West LA site is much higher with a mean of 0.79 ± 0.02, especially for the first fifteen model years. After the first fifteen model years the reducing capacity of the catalyst begins to decline and the data from all of the sites, while noisy due to a shrinking number of vehicles, starts to merge and decrease at similar rates.

The West LA site is a traffic light controlled freeway on-ramp that not only encourages accelerations, but most often after a stop by the vehicle. When the data for each site are compared from Tables 3, 6 and 9 the West LA site has the newest fleet, experiences the highest mean acceleration rates and has the highest mean NO emissions. All of these factors positively influence the higher mean NH$_3$ emissions seen at the West LA site and emphasizes the importance of driving mode on ammonia measurements.

On-road ammonia emissions have been previously reported by Baum *et al.* for a Los Angeles site of 0.35 g/kg in 1999 and by Burgard *et al.* in 2005 from gasoline-powered vehicles to be 0.47 ± 0.02 and 0.51 ± 0.01 for sites in Denver and Tulsa.[26, 27] The Denver and Tulsa measurement sites where curved uphill interchange ramps that had similar driving modes to those observed in San Jose and Fresno.

Figure 32 shows the mass in g/kg of NO$_x$ and NH$_3$ emissions against model year for the last 20 model years. NO$_x$ emissions have been calculated by converting the measured gNO/kg into gNO$_2$/kg and summing with the measured gNO$_2$/kg emissions. The gNO$_x$/kg means have been plotted on a scale that generally allows them to overlap with the gNH$_3$/kg emissions to highlight the similar emissions trends. In San Jose and Fresno the NH$_3$ and NO$_x$ emissions are decreasing
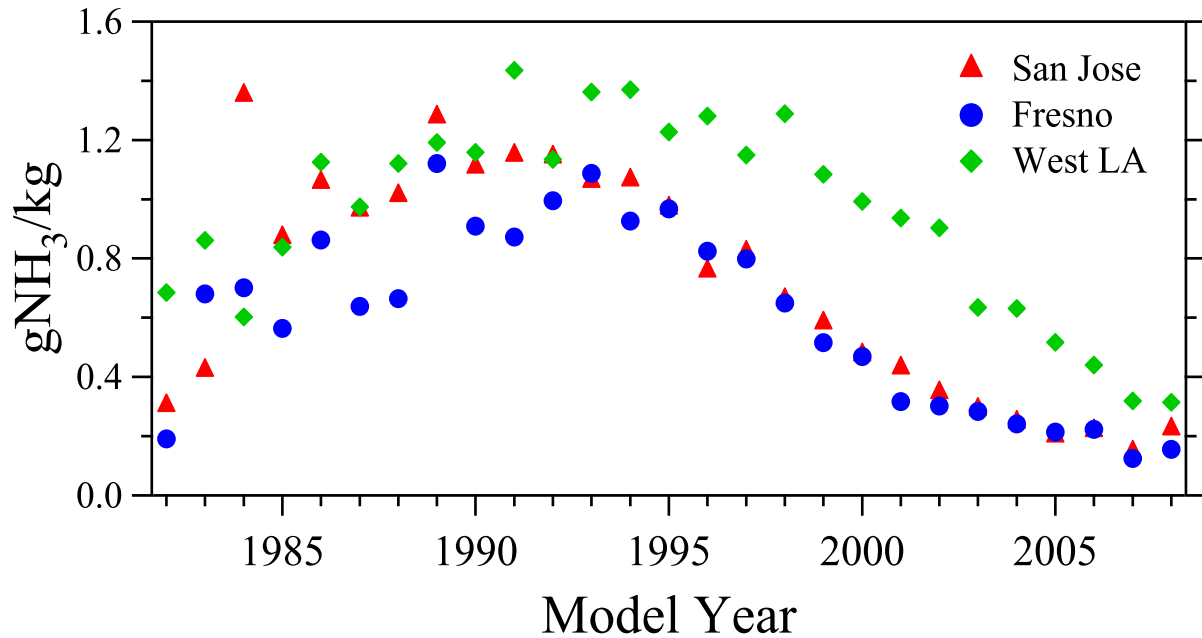
Figure 31. gNH3/kg emission averages as a function of model year for the three measurement sites.

at a similar rate over the latest 10 model years. At the West LA site some of the NO_x emissions appear to be depressed by higher NH_3 emissions for the newest model years. When the reducing capabilities of the catalytic converters diminish the NO_x emissions dominate and reflect the higher driving loads observed at the West LA site.

The percent ammonia of the total fixed nitrogen was analyzed to see if the percentage of ammonia increased while the total fixed nitrogen decreased with age, as shown in the Burgard *et al.* analysis of the Tulsa and Denver fleets.[27] The gNO$_x$/kg was calculated by converting gNO/kg to gNO$_2$/kg and summing the two. The percent of ammonia in the total fixed nitrogen, in g/kg, was calculated as shown by Burgard *et al.*[27] All of the N factors were converted to mole/kg.

$$\text{Molar \% NH}_3 \text{ in total fixed nitrogen } = \frac{100 \text{ x N}_{NH_3}}{N_{NH_3} + N_{NO_x}} \qquad (5)$$

Figure 33 shows the results of these calculations for each of the three sites. The molar %NO$_x$ and %NH$_3$ add to 100% and are percentages of the gN$_2$/kg values plotted by model year. The noise increases for the molar percentages in newest model years because of the diminishing amount of fixed nitrogen emissions. The total fixed nitrogen species have decreased over the last 20 model years, however, the percent contributed by ammonia (the circles) has increased. Again driving mode is a significant contributor to the differences in the amount of fixed nitrogen being emitted with the West LA site having a steeper increase and higher levels of fixed nitrogen.

A small fraction of the total nitrogen emissions is composed of NO$_2$ emissions. While all of the oxidized nitrogen in an engine begins life as NO in some diesel engines the exhaust cools rapidly

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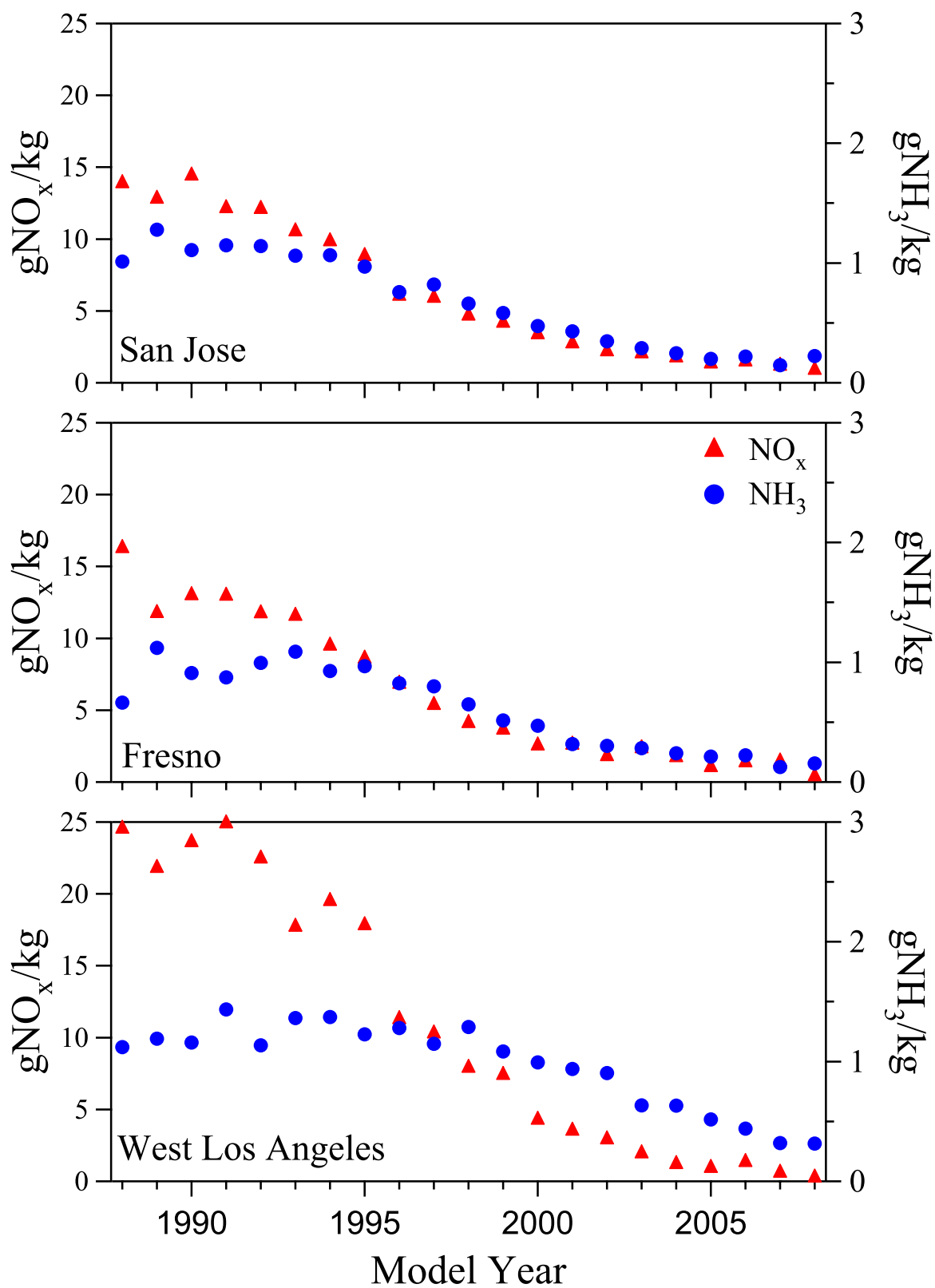
Figure 32. Mean gNO_x/kg (triangles, left axis) and gNH_3/kg (circles, right axis) emissions as a function of model year for the three measurement sites.
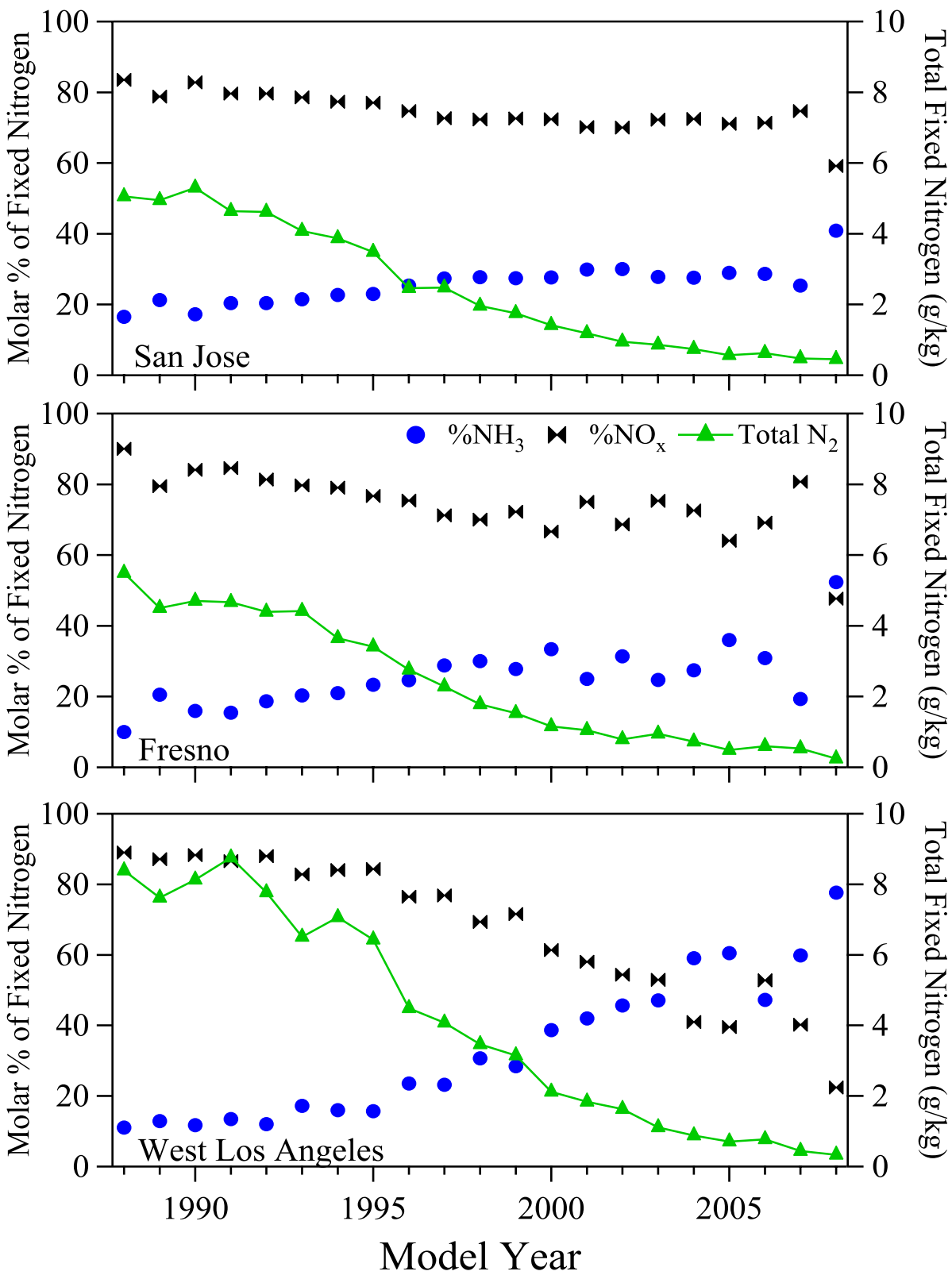
Figure 33. Total fixed nitrogen in g/kg (triangles, right axis) with the molar percent composition distributed between the NO_x (bowties, left axis) component and the NH_3 component (circles, left axis).

enough in the presence of oxygen that 5 to 8% of the NO will be further oxidized to NO_2 before it is emitted from the tailpipe. Figure 34 is a graph of NO_2 emissions from each of the three measurements sites plotted against model year. Unfortunately the license plate match that we obtained from the state did not contain fuel type and we are unable to separate the gasoline and diesel powered vehicles. What we can say is that in 2005 data collected at the West LA site had 2.5% of the measurements from diesel powered vehicles.[28] Because of the large agricultural presence in California's central valley it is reasonable to expect more diesel trucks in the Fresno fleet but we cannot be certain without the fuel information.
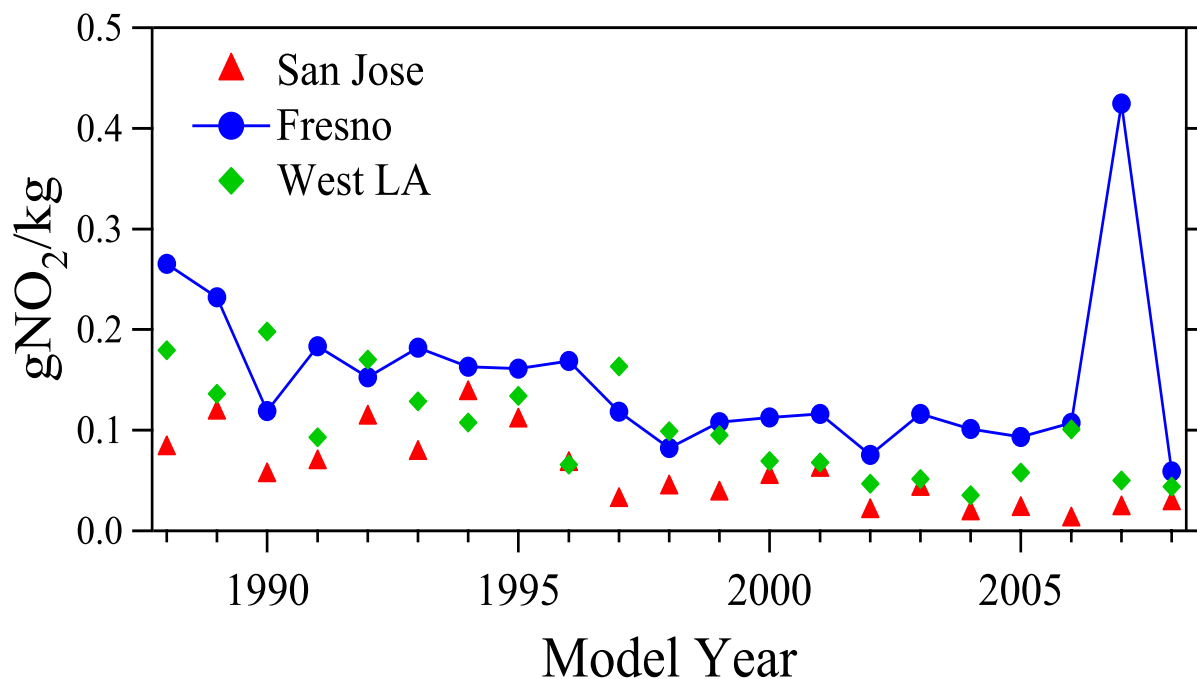
Figure 34. Mean gNO_2/kg emissions versus model year for the three California measurement sites.

In general the emissions versus model year comparison are uninteresting with most of the data being at low levels with a slight but noisy increase in the older model years. Differences between sites likely reflect differences in the composition of diesel vehicles. The exception is a single model year from the Fresno location. While the 2007 model year certainly satisfies many of the requirements for it to be labeled an outlier, this data point is not an outlier and can be explained. The location of the Fresno measurements, quite by happen stance, was included in the local return route for an ambulance company servicing the downtown Health Center. The 2007 model year data set contains 30 Dodge Sprinter vans (a total of 57 measurements out of 872 total measurements), 29 of which were in service as ambulances. Each of these Sprinter vans has a 3.0l diesel engine equipped with a standard diesel particulate filter. The filter is regenerated with an upstream oxidation catalyst that converts NO to NO_2 which in turn oxidizes the accumulated particles in the filter. Any imbalance between the production of NO_2 and particulate accumulation levels can result in the direct emissions of NO_2. We believe that scenario, an excess generation of NO_2, is what we have observed at the Fresno site.

Table 12 summarizes some of the measurement statistics for the 2007 model year vehicles. The Sprinters are higher for NO and NO_2, however, diesel powered vehicles in general will have higher levels of these two species when compared with gasoline powered vehicles. What distinguishes this set of diesel vehicles is the fact that 60% of the NO_x emissions are emitted as NO_2 and the level of NO_x emissions is significant (the mean gNO_x/kg for the entire Fresno fleet is 4.5). The Sprinters only account for 0.4% of all of the Fresno measurements but 14.8% of the NO_2 measured at this site. In addition we contacted the ambulance service and found out that their average yearly mileage for their fleet is 50,000 miles/year/ambulance. If the NO_2 emissions we observed are used as a yearly average and these vehicles are estimated to have a fuel economy of 20 mpg (6.25 mpkg assuming a fuel density of 3200g/gallon) then each ambulance can be expected to emit approximately 0.04 metric tonnes of NO_2/year per ambulance.

Table 12. Emission measurements for 2007 model year vehicles measured in Fresno.

Grouping	Measurements	Mean gNO / kg	Mean gNO_2 / kg	Mean gNO_x / kg	Ratio NO_2 / NO
Sprinters	57	2.05	4.85	7.99	2.4
All Others	815	0.56	0.12	0.95	0.2

These Sprinter vans should focus our attention on a potentially new air quality issue which is the direct emissions of NO_2 in the urban air mass. Prior to the national regulations for reducing particulate matter from diesel vehicles, direct emissions of NO_2 from diesel vehicles, whether light or heavy-duty, were generally limited by thermodynamics to less than 10% of the tailpipe emitted NO_x (gasoline vehicles generally emit less than 1% of their tailpipe NO_x as NO_2). As self regenerating particulate filters become common in the diesel fleet current research indicates that a much larger fraction of the tailpipe NO_x emissions will be emitted as NO_2. We have collected measurements from heavy-duty trucks in the South Coast Air Basin that shows 2007 and 2008 engines emitting NO_2/NO_x ratios of 0.31 and 0.55 compared to an average of 0.07 for all prior years.[29] It is generally believed that as total tailpipe NO_x emissions decrease with the introduction 0.2 g/bhp-hr 2010 engines that direct NO_2 emissions, even if they are a larger fraction, will also be reduced. We can hope that this will be the case, however, previous tightening of the diesel NO_x regulations have not translated into similar on-road reductions.[30, 31]

Fleet SO_2 emissions should be largely controlled by the amount of sulfur present in the fuel with a small increase in older vehicles on account of oil consumption. For California gasoline and diesel fuels are limited to 15ppmw sulfur or approximately 0.03 gSO_2/kg. Figure 35 is the plot of the mean gSO_2/kg by model year for each of the three measurement sites. We do not expect to see any model year dependence for SO_2, however, a very strong model year dependence is seen at all of the sites. In general the first eight model years (2001 – 2008) are at or below the 0.03 gSO_2/kg level if the fuel is the only source of sulfur. After the 2001 model year all of the sites show a steady increase to levels that cannot be fully reconciled by the fuel and or additional oil consumption. The model year dependence of course correlates with a number of other species present in vehicle exhaust and suggests some type of interference in our fitting algorithms for SO_2.
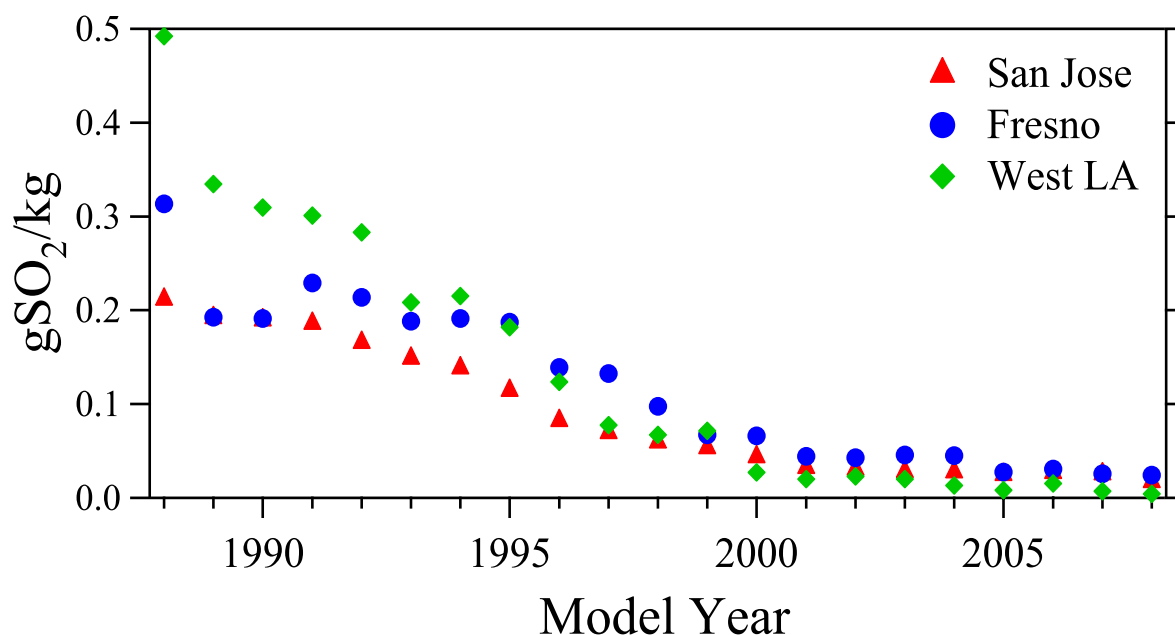
Figure 35. Mean gSO_2/kg emissions as a function of model year of each of the three measurement sites.

SUMMARY AND CONCLUSIONS

The University of Denver has completed an on-road remote sensing study of motor vehicle emissions at sites in San Jose, Fresno and Los Angeles California. This is the first time that US light-duty fleets have been measured with our new multi-spectrometer instrument. A database for each site was compiled and contains 24,978 records in San Jose, 13,365 records in Fresno and 17,953 records in West Los Angeles for which the State of California provided registration information. All of these records contained valid measurements for at least CO and CO_2, and most of the remaining records contained valid measurements for HC, NO, SO_2, NH_3 and NO_2 as well.

Previous measurements existed at the San Jose site (1999) and the West Los Angeles site (1999, 2001, 2003 and 2005). The mean CO, HC and NO emissions for the fleet measured in San Jose experienced large reduction for all three species. At the West Los Angeles site previous reductions in CO and HC continued with this study, however, NO emissions increased from the 2005 measurements. Whether the increase in NO emissions is related to the change of season (fall to spring) that the measurements were collected is unclear and cannot be ruled out. The Fresno site had the oldest fleet at approximately 8.5 years old and is the only site where new car sales never recovered after the 2001 downturn.

Ammonia emissions are influenced by driving mode and we observed differences between the three sites that were sampled. San Jose and Fresno had very similar ammonia emissions with means of 0.48 ± 0.01 and 0.49 ± 0.01 while the data collected at the West Los Angeles site was much higher with a mean of 0.79 ± 0.02. The West Los Angeles site had significantly higher emissions for the newest model year vehicles and we believe that is a combination of the more

aggressive driving mode and the newer fleet (the youngest of the three sites at approximately 7.3 years old). We also observed that once the reducing capacity of the catalyst starts to wane (around 15 years), driving mode becomes less important as all of the sites ammonia emissions retreat with age at a similar rate. As NO_x emissions have decreased over the last twenty model years the amount of the total fixed nitrogen emissions have also decreased. However, the fraction of these fixed nitrogen emissions contributed by ammonia have increased.

Light-duty measurements of NO_2 were generally expected to be rather uninteresting as gasoline powered vehicles emit little if any NO_2 and the fraction of the light-duty fleet in California that are diesels is small. However, beginning with the 2007 model year vehicles diesel engine manufacturers were required to begin phasing in major reductions in particulate and NO_x emissions with the full phase-in to be complete in 2010. These new regulations affect all diesel powered vehicles not just heavy-duty diesel vehicles. At the Fresno location a local ambulance company, which happened to use our ramp for their return trip from the downtown health center, provided us with measurements from new diesel particulate filter equipped vans. In total 30 2007 Dodge Sprinter vans (29 operating as ambulances) were measured 57 times over the seven days of measurements. These vans had gNO_2/kg emissions that were an order of magnitude larger than the other 865 2007 vehicles. These vehicles also had more than twice of their NO_x emissions emitted as NO_2 and while only counting for 0.4% of all the measurements they accounted for almost 15% of the NO_2 emissions. While the number of diesel vehicles in Fresno is small the increased NO_2 emissions seen from these vehicles on-road might point to a future of increased on-road NO_2 emissions. This would have large ramifications for local ozone formation.

Sulfur dioxide emissions were also recorded with our new instrument and despite changes to the analysis software they still indicate a model year dependence that we do not fully understand. Sulfur dioxide emissions should be limited to the amount of sulfur in the fuel plus a small additional amount in older vehicles due to oil consumption. This should be reflected with most model years being at or below the fuel sulfur levels (15ppmw which translates into approximately 0.03g SO_2/kg). We find only the first eight to nine model years that meet these levels with later models rising to higher levels that are inconsistent with the known amounts of sulfur available for oxidation. The most logical explanation for these higher sulfur levels is some type of interference found in older vehicle exhaust that positively interferes with our SO_2 measurements. At this time we have been unable to identify this interference.

RECOMMENDATIONS

Remote vehicle exhaust sensors are capable of quickly collecting a large number of emission measurements that can be used to track fleet emission trends. NH_3, while currently unregulated, is one important atmospheric species that little is known about its long term trend in the US vehicle fleet. The current project establishes a baseline for NH_3 emissions. To understand the trend, follow-up surveys need to be conducted in the future, preferably at the same time of year and locations.

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COMMON ACRONYMS

CH_2 – Generic formula for gasoline
CO – Carbon monoxide
CO_2 – Carbon dioxide
CRC – Coordinating Research Council
EPA – Environmental Protection Agency
FEAT – Fuel Efficiency Automobile Test
FID – Flame Ionization Detector
HC – Hydrocarbons
I/M – Inspection and Maintenance
IMRC – California Inspection and Maintenance Review Committee
IR – Infrared
MY– Model Year
NDIR – Non-Dispersive Infrared
NH_3 – Ammonia
NO – Nitric Oxide
NO_2 – Nitrogen dioxide
NO_x – Nitrogen oxides
ppm – Parts per million
ppmw – Parts per million by weight
SO_2 – Sulfur dioxide
UV – Ultraviolet
VIN – Vehicle Identification Number
VSP – Vehicle Specific Power

APPENDIX A: FEAT criteria to render a reading "invalid" or not measured.

Not measured:

1) Beam block and unblock and then block again with less than 0.5 seconds clear to the rear. Often caused by elevated pickups and trailers causing a "restart" and renewed attempt to measure exhaust. The restart number appears in the database.

2) Vehicle which drives completely through during the 0.4 seconds "thinking" time (relatively rare).

Invalid :

1) Insufficient plume to rear of vehicle relative to cleanest air observed in front or in the rear; at least five, 10ms averages >0.25% CO_2 in 8 cm path length. Often heavy-duty diesel trucks, bicycles.

2) Excessive error on CO/CO_2 slope, equivalent to $\pm$20% for %CO. >1.0, 0.2%CO for %CO<1.0.

3) Reported %CO , <-1% or >21%. All gases invalid in these cases.

4) Excessive error on HC/CO_2 slope, equivalent to $\pm$20% for HC >2500ppm propane, 500ppm propane for HC <2500ppm.

5) Reported HC <-1000ppm propane or >40,000ppm. HC "invalid".

6) Excessive error on NO/CO_2 slope, equivalent to $\pm$20% for NO>1500ppm, 300ppm for NO<1500ppm.

7) Reported NO <-700ppm or >7000ppm. NO "invalid".

8) Excessive error on SO_2/CO_2 slope, equivalent to $\pm$40ppm.

9) Reported SO_2 < -80ppm or > 7000ppm. SO_2 "invalid".

10) Excessive error on NH_3/CO_2 slope, equivalent to $\pm$50ppm.

11) Reported NH_3 < -80ppm or > 7000ppm. NH3 "invalid".

12) Excessive error on NO_2/CO_2 slope, equivalent to $\pm$20% for NO_2 > 200ppm, 40ppm for NO_2 < 200ppm

13) Reported NO_2 < -500ppm or > 7000ppm. NO_2 "invalid".

Speed/Acceleration valid only if at least two blocks and two unblocks in the time buffer and all blocks occur before all unblocks on each sensor and the number of blocks and unblocks is equal on each sensor and 100mph>speed>5mph and 14mph/s>accel>-13mph/s and there are no restarts, or there is one restart and exactly two blocks and unblocks in the time buffer.

APPENDIX B: Database Format.

There are three databases, one for each location. Sanjos08.dbf, Fresno08.dbf, Labrea08.dbf are Microsoft FoxPro database files, and can be opened by any version of MS FoxPro. The files can also be read by a number of other database management programs as well, and they are available from our website at www.feat.biochem.du.edu. The following is an explanation of the data fields found in this database:

License   California license plate.

Date   Date of measurement, in standard format.

Time   Time of measurement, in standard format.

Percent_CO Carbon monoxide concentration, in percent.

CO_err   Standard error of the carbon monoxide measurement.

Percent_HC Hydrocarbon concentration (propane equivalents), in percent.

HC_err   Standard error of the hydrocarbon measurement.

Percent_NO Nitric oxide concentration, in percent.

NO_err   Standard error of the nitric oxide measurement.

PercentSO2 Sulfur dioxide concentration, in percent.

SO2_err   Standard error of the sulfur dioxide measurement.

PercentNH3 Ammonia concentration, in percent.

NH3_err   Standard error of the ammonia measurement.

PercentNO2 Nitrogen dioxide concentration, in percent.

NO2_err   Standard error of the nitrogen dioxide measurement.

PercentCO2 Carbon dioxide concentration, in percent.

CO2_err   Standard error of the carbon dioxide measurement.

Opacity   Opacity measurement, in percent.

Opac_err   Standard error of the opacity measurement.

Restart   Number of times data collection is interrupted and restarted by a close-following vehicle, or the rear wheels of tractor trailer.

HC_flag   Indicates a valid hydrocarbon measurement by a "V", invalid by an "X".

NO_flag   Indicates a valid nitric oxide measurement by a "V", invalid by an "X".

SO2_flag   Indicates a valid sulfur dioxide measurement by a "V", invalid by an "X".

NH3_flag   Indicates a valid ammonia measurement by a "V", invalid by an "X".

NO2_flag   Indicates a valid nitrogen dioxide measurement by a "V", invalid by an "X".

Opac_flag   Indicates a valid opacity measurement by a "V", invalid by an "X".

Max_CO2   Reports the highest absolute concentration of carbon dioxide measured by the remote sensor over an 8 cm path; indicates plume strength.

Speed_flag Indicates a valid speed measurement by a "V", an invalid by an "X", and slow speed (excluded from the data analysis) by an "S".

Speed   Measured speed of the vehicle, in mph.

Accel   Measured acceleration of the vehicle, in mph/s.

Tag_name   File name for the digital picture of the vehicle.

Exp_date   License expiration date.

Year   Model year.

Make   Manufacturer of the vehicle.

Vin   Vehicle identification number.

County   California county number vehicle is registered in (not available for Fresno data).

APPENDIX C: Temperature and Humidity Data

Data collected at the San Jose International Airport

	**1999 San Jose Temperature and Humidity Data**								
Time	10/25 °F	10/25 %RH	10/26 °F	10/26 %RH	10/27 °F	10/27 %RH	10/28 °F	10/28 %RH	10/29 °F	10/29 %RH
6:53	54	87	53	89	55	90	59	94	48	83
7:53	55	84	54	93	58	81	59	94	53	77
8:53	56	75	57	87	64	68	59	94	56	70
9:53	59	63	59	83	70	59	63	70	55	72
10:53	64	55	60	84	72	57	63	70	63	51
11:53	67	44	64	68	74	54	63	68	65	45
12:53	70	39	65	66	76	52	64	67	67	40
13:53	70	53	66	65	79	49	64	67	69	41
14:53	69	61	66	68	72	61	67	53	70	37
15:53	67	70	62	78	73	59	63	50	70	37
16:53	63	75	60	80	69	68	62	44	65	54
17:53	59	87	53	89	66	75	59	58	62	58

	**2008 San Jose Temperature and Humidity Data**							
Time	3/04 °F	3/04 %RH	3/05 °F	3/05 %RH	3/06 °F	3/06 %RH	3/07 °F	3/07 %RH
8:53	51	59	56	47	50	61	52	61
9:53	56	53	60	32	55	51	55	57
10:53	59	50	62	32	59	44	58	53
11:53	64	43	65	26	62	41	62	45
12:53	65	40	66	29	61	48	65	37
13:53	65	49	66	27	64	38	67	32
14:53	66	45	67	28	64	42	66	45
15:53	65	45	66	29	60	60	65	32
16:53	64	40	65	30	57	67	63	33
17:53	60	46	58	49	57	64	61	44

Data Collected at the Fresno Yosemite International Airport

2008 Fresno Temperature and Humidity Data								
Time	3/08 °F	3/08 %RH	3/09 °F	3/09 %RH	3/10 °F	3/10 %RH	3/11 °F	3/11 %RH
6:53	48	83	47	80	48	74	51	74
7:53	51	77	49	77	54	62	55	64
8:53	55	69	55	67	59	54	58	62
9:53	60	56	61	52	64	43	61	58
10:53	65	43	62	48	68	38	65	52
11:53	66	40	65	43	71	31	68	47
12:53	67	40	67	40	74	27	71	38
13:53	68	39	69	36	75	22	72	37
14:53	68	41	70	34	76	23	70	46
15:53	68	42	71	33	75	24	69	46
16:53	67	40	71	30	75	26	68	47
17:53	64	47	69	32	71	35	67	51

2008 Fresno Temperature and Humidity Data								
Time	3/12 °F	3/12 %RH	3/13 °F	3/13 %RH	3/14 °F	3/14 %RH		
6:53	51	86	56	67	47	83		
7:53	51	86	57	72	50	74		
8:53	55	80	58	70	54	67		
9:53	61	65	61	65	56	60		
10:53	63	65	64	54	58	49		
11:53	66	54	66	59	60	44		
12:53	69	49	68	59	60	43		
13:53	71	43	70	53	62	40		
14:53	71	41	70	49	63	35		
15:53	71	43	70	46	62	37		
16:53	69	41	69	44	61	38		
17:53	65	54	65	47	59	41		

Data Collected at the Los Angeles International Airport

	1999 West Los Angeles Temperature and Humidity Data									
Time	11/09 °F	11/09 %RH	11/10 °F	11/10 %RH	11/11 °F	11/11 %RH	11/12 °F	11/12 %RH	11/13 °F	11/13 %RH
5:50	54	87	53	93	52	89	58	93	56	100
6:50	55	80	55	83	57	75	57	100	57	100
7:50	57	78	57	81	60	70	59	96	58	100
8:50	60	72	61	70	63	65	59	90	59	93
9:50	63	68	64	63	67	59	62	84	61	84
10:50	66	61	65	66	68	59	61	87	61	84
11:50	68	55	65	70	68	61	62	84	61	84
12:50	67	66	64	75	68	63	61	84	62	81
13:50	64	73	64	75	69	57	62	81	62	81
14:50	64	75	64	70	67	66	62	84	62	81
15:50	62	81	64	68	65	76	61	87	62	81
16:50	61	84	63	73	63	81	61	90	61	87

	2001 West Los Angeles Temperature and Humidity Data									
Time	10/15 °F	10/15 %RH	10/16 °F	10/16 %RH	10/17 °F	10/17 %RH	10/18 °F	10/18 %RH	10/19 °F	10/19 %RH
8:03	64	90	66	90	61	90	62	93	64	84
9:03	67	87	66	81	63	87	65	78	67	76
10:03	68	79	69	73	65	78	70	64	69	73
11:03	71	73	70	71	67	73	69	73	68	76
12:03	68	68	67	79	67	73	70	68	66	78
13:03	69	76	69	73	66	75	69	70	66	78
14:03	69	76	68	76	67	76	70	66	63	84
15:03	67	76	68	76	66	78	68	70	64	84
16:03	65	84	66	81	65	81	67	79	63	87
17:03	63	87	64	90	63	87	64	87	63	87
18:03	63	93	63	90	62	90	63	90	62	90

2003 West Los Angeles Temperature and Humidity Data									
Time	10/27 °F	10/27 %RH	10/28 °F	10/28 %RH	10/29 °F	10/29 %RH	10/30 °F	10/30 %RH	10/31 °F	10/31 %RH
7:50	71	31	69	41	64	87	64	73	57	78
8:50	78	24	75	33	66	81	64	73	58	72
9:50	84	21	79	30	68	73	65	70	61	56
10:50	87	24	81	29	69	70	67	66	62	56
11:50	84	29	80	41	67	81	66	59	62	58
12:50	82	27	75	58	69	76	65	59	63	52
13:50	83	24	77	54	67	81	63	63	62	56
14:50	82	26	77	50	66	81	64	54	61	58
15:50	79	32	75	54	64	87	62	52	61	60
16:50	74	54	70	76	63	90	60	62	61	63
17:50	72	60	70	82	64	87	60	62	61	60
18:50	73	62	67	97	63	87	60	62	60	62

2005 West Los Angeles Temperature and Humidity Data									
Time	10/17 °F	10/17 %RH	10/18 °F	10/18 %RH	10/19 °F	10/19 %RH	10/20 °F	10/20 %RH	10/21 °F	10/21 %RH
7:50	65	81	59	93	61	84	61	87	61	90
8:50	66	84	60	93	63	78	63	84	62	86
9:50	67	76	61	87	63	81	65	81	64	84
10:50	67	79	62	84	65	76	67	76	64	84
11:50	66	78	64	78	66	70	68	73	63	87
12:50	64	87	65	70	66	70	68	73	63	87
13:50	60	93	63	78	67	68	66	81	64	84
14:50	60	93	63	78	65	73	64	87	62	90
15:50	60	93	62	81	64	78	61	93	62	90
16:50	60	93	62	78	62	84	61	93	61	93
17:50	60	90	61	84	61	90	60	96	61	90
18:50	60	86	61	84	61	90	60	96	61	93

Time	3/17 °F	3/17 %RH	3/18 °F	3/18 %RH	3/19 °F	3/19 %RH	3/20 °F	3/20 %RH	3/21 °F	3/21 %RH
7:50	59	13	56	49	55	77	57	69	57	62
8:50	63	14	60	56	58	70	58	67	63	48
9:50	67	9	63	46	61	60	58	70	66	42
10:50	69	10	67	36	59	67	59	67	69	32
11:50	66	17	65	50	60	65	60	65	70	41
12:50	66	28	64	48	60	65	59	70	69	44
13:50	65	24	63	52	60	65	60	67	69	41
14:50	63	26	61	63	58	70	60	70	69	39
15:50	62	28	60	67	57	72	60	67	67	39
16:50	62	22	59	65	55	77	60	70	67	40
17:50	59	20	58	72	54	80	60	70	66	43
18:50	57	11	57	78	54	80	58	75	63	56

2008 West Los Angeles Temperature and Humidity Data

APPENDIX D: Example Calculation of Vehicle Specific Power Adjusted Vehicle Emissions

1997 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	236	225	53200
	0	224	1609	360090
	5	307	4985	1531000
	10	431	6146	2648020
	15	548	2624	1438060
	20	590	456	269180
			16045	6299550
			Mean NO (ppm)	**393**
1998 (Measured)	VSP Bin	Mean NO (ppm)	No. of Measurements	Total Emissions
	-5	233	137	31951
	0	239	784	187394
	5	265	3613	956613
	10	385	6685	2576433
	15	475	6012	2856195
	20	483	2392	1156320
			19623	7764906
			Mean NO (ppm)	**396**
1998 (Adjusted)	VSP Bin	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	-5	233	225	52474
	0	239	1609	384588
	5	265	4985	1319877
	10	385	6146	2368700
	15	475	2624	1246616
	20	483	456	220436
			16045	5592691
			Mean NO (ppm)	**349**

Note that the Mean NO readings listed here have been rounded to the nearest ppm values which results in the Total Emissions column appearing to not be a direct multiplication product. The -5 to 20 kw/tonne bins are chosen to preclude any "off-cycle" emissions.

The object of this adjustment is to have the 1998 fleet's emissions calculated as if they drove (VSP wise) like the 1997 fleet. This is accomplished by first binning and averaging the 1997 and 1998 data (the top two tables). We then combine the mean NO values from the 1998 fleet with the numerical VSP bin distribution from the 1997 fleet in the bottom table. The product of these two columns is summed and the sum total emissions are divided by the number of 1997 vehicles to produce the 1998 adjusted mean NO average. For this example, it shows that the 1998 fleet when driven like the 1997 fleet has lower NO emissions than the 1997 fleet.

APPENDIX E: Example Calculation of Model Year Adjusted Fleet Emissions

1997 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	690	398	274620
	84	720	223	160560
	85	680	340	231200
	86	670	513	343710
	87	690	588	405720
	88	650	734	477100
	89	610	963	587430
	90	540	962	519480
	91	500	1133	566500
	92	450	1294	582300
	93	460	1533	705180
	94	370	1883	696710
	95	340	2400	816000
	96	230	2275	523250
	97	150	2509	376350
			17748	7266110
			Mean NO (ppm)	**409**

1998 (Measured)	Model Year	Mean NO (ppm)	No. of Measurements	Total Emissions
	83	740	371	274540
	84	741	191	141531
	85	746	331	246926
	86	724	472	341728
	87	775	557	431675
	88	754	835	629590
	89	687	1036	711732
	90	687	1136	780432
	91	611	1266	773526
	92	538	1541	829058
	93	543	1816	986088
	94	418	2154	900372
	95	343	2679	918897
	96	220	2620	576400
	97	177	3166	560382
			20171	9102877
			Mean NO (ppm)	**451**

1998 (Adjusted)	Model Year	'98 Mean NO (ppm)	'97 No. of Meas.	Total Emissions
	83	740	398	294520
	84	741	223	165243
	85	746	340	253640
	86	724	513	371412
	87	775	588	455700
	88	754	734	553436
	89	687	963	661581
	90	687	962	660894
	91	611	1133	692263
	92	538	1294	696172
	93	543	1533	832419
	94	418	1883	787094
	95	343	2400	823200
	96	220	2275	500500
	97	177	2509	444093
			17748	8192167
			Mean NO (ppm)	**462**

APPENDIX F: Field Calibration Records.

2008 San Jose (FEAT 3002)							
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	SO_2 Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
3/4	10:15	1.46	1.28	1.40	0.89	1.07	1.05
3/4	15:30	1.29	1.09	1.17	0.78	1.07	0.83
3/5	9:55	1.32	1.15	1.09	1.17	1.02	0.89
3/5	13:20	1.25	1.12	0.97	1.10	1.02	0.66
3/6	9:45	1.52	1.32	1.32	1.27	1.04	0.99
3/7	9:40	1.71	1.49	1.76	1.09	10.3	0.88
3/7	13:05	1.40	1.23	1.41	1.06	10.3	0.53

2008 Fresno (FEAT 3002)							
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	SO_2 Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
3/8	12:10	1.41	1.25	1.11	0.87	1.01	0.75
3/9	9:25	1.87	1.69	1.58	0.95	1.01	1.32
3/9	11:25	1.54	1.41	1.31	1.25	1.01	0.56
3/10	7:25	2.29	2.07	1.90	1.85	1.01	2.01
3/10	9:20	1.75	1.60	1.36	1.43	1.01	1.23
3/10	14:10	1.33	1.22	0.96	0.99	1.01	0.93
3/11	7:45	2.01	1.84	1.64	1.74	1.02	1.71
3/11	9:10	1.81	1.64	1.37	1.54	1.02	1.43
3/11	14:20	1.45	1.22	1.25	1.21	1.02	1.30
3/12	7:30	2.27	2.16	1.72	1.11	0.99	1.71
3/12	9:50	1.85	1.69	1.40	1.28	0.99	1.39
3/12	12:30	1.54	1.40	1.02	1.06	0.99	1.01
3/12	14:40	1.37	1.26	0.90	1.02	0.99	0.85
3/13	7:20	2.04	1.83	1.67	1.73	0.94	1.49
3/13	10:00	1.72	1.55	1.27	1.52	0.94	1.13
3/13	12:30	1.55	1.35	1.14	1.26	0.94	1.02
3/13	14:20	1.46	1.25	1.06	1.13	0.94	0.95
3/14	7:25	2.02	1.87	1.56	1.15	0.93	1.74
3/14	9:15	1.70	1.57	1.32	1.03	0.93	1.47
3/14	12:10	1.50	1.41	1.11	1.06	0.93	1.24

2001 West Los Angeles (FEAT 3002)				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
10/15	8:00	1.56	1.40	2.01
10/15	13:00	1.22	1.05	1.26
10/16	7:00	1.47	1.25	1.85
10/16	15:30	1.23	1.02	1.39
10/17	7:00	1.47	1.50	2.30
10/17	12:50	1.39	1.12	1.53
10/18	8:30	2.17	1.87	2.67
10/18	10:55	1.63	1.46	2.02
10/19	7:55	1.68	1.39	1.42
10/19	10:09	1.50	1.26	1.31

2003 West Los Angeles (FEAT 3002)				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
10/27	12:30	1.228	1.27	2.14
10/27	17:20	1.333	1.19	1.7
10/28	8:00	3.14	2.91	7.2
10/28	9:45	2.22	2.2	4.87
10/28	11:23	1.6	1.5	2.53
10/29	7:50	1.666	1.47	1.89
10/29	11:30	1.31	1.15	1.42
10/29	14;20	1.31	1.14	1.228
10/29	17:30	1.41	1.28	1.62
10/30	6:05	1.48	1.35	2.53
10/30	9:30	1.41	1.29	2.03
10/30	14:30	1.42	1.28	1.73
10/31	5:50	1.55	1.35	2.85
10/31	10:35	1.34	1.19	1.79

2005 West Los Angeles (FEAT 3002)				
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor
10/17	8:18	1.8	1.5	1.4
10/17	12:18	1.37	1.17	1.46
10/18	9:45	1.82	1.36	1.53
10/18	13:20	1.7	1.17	1.32
10/19	6:17	2.74	1.94	2.04
10/19	8:40	2.15	1.65	1.83
10/19	12:30	1.66	1.17	1.4
10/20	6:18	2.45	1.84	1.84
10/20	8:30	2.64	2.00	1.89
10/20	11:30	1.66	1.26	1.28
10/21	6:20	1.76	1.26	1.55
10/21	8:31	2.06	1.55	1.94
10/21	11:33	1.65	1.17	1.4

2008 West Los Angeles (FEAT 3002)						
Date	Time	CO Cal Factor	HC Cal Factor	NO Cal Factor	SO_2 Cal Factor	NH_3 Cal Factor	NO_2 Cal Factor
3/17	9:10	1.68	1.60	1.24	1.16	1.02	1.07
3/17	12:00	1.46	1.41	1.10	1.04	1.02	0.95
3/18	7:15	3.15	2.83	3.06	2.52	0.92	2.39
3/18	9:05	1.93	1.63	1.74	1.01	0.92	1.35
3/18	12:30	1.45	1.28	1.22	0.75	0.92	0.95
3/19	7:20	2.65	2.30	1.63	2.13	0.91	0.90
3/19	9:50	1.96	1.87	1.18	1.57	0.91	0.66
3/19	13:00	1.65	1.55	0.92	1.21	0.90	0.96
3/20	7:00	1.99	1.85	1.38	1.61	0.87	1.19
3/20	9:15	1.82	1.74	1.18	1.34	0.87	1.02
3/20	13:15	1.51	1.44	1.00	1.16	0.87	0.86
3/21	7:15	3.50	3.40	2.70	3.10	0.85	2.08
3/21	8:25	2.81	2.70	1.92	2.20	0.85	1.48
3/21	9:35	2.02	1.98	1.26	1.53	0.85	0.92
3/21	11:45	1.70	1.65	1.10	1.22	0.85	0.80